PATENT COOPERATION TREATY

PCT

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

From the INTERNATIONAL BUREAU

To:

Assistant Commissioner for Patents
United States Patent and Trademark
Office
Box PCT
Washington, D.C.20231
ETATS-UNIS D'AMERIQUE

in its capacity as elected Office

Date of mailing (day/month/year) 23 October 2000 (23.10.00)	
International application No. PCT/AU00/00208	**Applicant's or agent's file reference**
International filing date (day/month/year) 17 March 2000 (17.03.00)	**Priority date** (day/month/year) 19 March 1999 (19.03.99)
Applicant ROSENBERG, Steven, Philip et al	

1. The designated Office is hereby notified of its election made:

   [X] in the demand filed with the International Preliminary Examining Authority on:

   21 September 2000 (21.09.00)

   [ ] in a notice effecting later election filed with the International Bureau on:

2. The election [X] was

   [ ] was not

   made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland	Authorized officer Nestor Santesso
Facsimile No.: (41-22) 740.14.35	Telephone No.: (41-22) 338.83.38

Form PCT/IB/331 (July 1992)

AU0000208

PATENT COOPERATION TREATY

PCT

INFORMATION CONCERNING ELECTED OFFICES NOTIFIED OF THEIR ELECTION

(PCT Rule 61.3)

From the INTERNATIONAL BUREAU

To:

VAN WOLLINGEN, Rolf
Griffith Hack
256 Adelaide Terrace
Perth, W.A. 6000
AUSTRALIE

GHIPS MATTER
No. FP12532

Date of mailing (day/month/year)	
23 October 2000 (23.10.00)	

Applicant's or agent's file reference	IMPORTANT INFORMATION

International application No.	International filing date (day/month/year)	Priority date (day/month/year)
PCT/AU00/00208	17 March 2000 (17.03.00)	19 March 1999 (19.03.99)

Applicant

WORSLEY ALUMINA PTY. LTD. et al

1. The applicant is hereby informed that the International Bureau has, according to Article 31(7), notified each of the following Offices of its election:

    AP :GH,GM,KE,LS,MW,SD,SL,SZ,TZ,UG,ZW
    EP :AT,BE,CH,CY,DE,DK,ES,FI,FR,GB,GR,IE,IT,LU,MC,NL,PT,SE
    National :AG,AU,BG,CA,CN,CZ,DE,DZ,IL,JP,KP,KR,MN,NO,NZ,PL,RO,RU,SE,SK,US

2. The following Offices have waived the requirement for the notification of their election; the notification will be sent to them by the International Bureau only upon their request:

    EA :AM,AZ,BY,KG,KZ,MD,RU,TJ,TM
    OA :BF,BJ,CF,CG,CI,CM,GA,GN,GW,ML,MR,NE,SN,TD,TG
    National :AE,AL,AM,AT,AZ,BA,BB,BR,BY,CH,CR,CU,DK,DM,EE,ES,FI,GB,GD,GE,GH,
    GM,HR,HU,ID,IN,IS,KE,KG,KZ,LC,LK,LR,LS,LT,LU,LV,MA,MD,MG,MK,MW,MX,PT,SD,
    SG,SI,SL,TJ,TM,TR,TT,TZ,UA,UG,UZ,VN,YU,ZA,ZW

3. The applicant is reminded that he must enter the "national phase" **before the expiration of 30 months from the priority date** before each of the Offices listed above. This must be done by paying the national fee(s) and furnishing , if prescribed, a translation of the international application (Article 39(1)(a)), as well as, where applicable, by furnishing a translation of any annexes of the international preliminary examination report (Article 36(3)(b) and Rule 74.1).

    Some offices have fixed time limits expiring later than the above-mentioned time limit. For detailed information about the applicable time limits and the acts to be performed upon entry into the national phase before a particular Office, see Volume II of the PCT Applicant's Guide.

    The entry into the European regional phase is postponed **until 31 months from the priority date** for all States designated for the purposes of obtaining a European patent.

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland	Authorized officer: Nestor Santesso
Facsimile No. (41-22) 740.14.35	Telephone No. (41-22) 338.83.38

Form PCT/IB/332 (September 1997)   3604620

REC'D **0 7 NOV 2000**

W!PO   PCT

Applicant's or agent's file reference RVW:NR:FP12532	**FOR FURTHER ACTION**	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416).

International application No. **PCT/AU00/00208**	International filing date *(day/month/year)* 17 March 2000	Priority Date *(day/month/year)* 19 March 1999

International Patent Classification (IPC) or national classification and IPC

Int. Cl.⁷   C01F 7/47, 7/06

Applicant
1.   WORSLEY ALUMINA PTY LTD et al

1.   This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2.   This REPORT consists of a total of   **4**   sheets, including this cover sheet.

☐   This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of   sheet(s).

3. This report contains indications relating to the following items:

I	☒	Basis of the report
II	☐	Priority
III	☐	Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
IV	☐	Lack of unity of invention
V	☒	Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
VI	☐	Certain documents cited
VII	☐	Certain defects in the international application
VIII	☐	Certain observations on the international application

Date of submission of the demand 21 September 2000	Date of completion of the report 19 October 2000

Name and mailing address of the IPEA/AU AUSTRALIAN PATENT OFFICE PO BOX 200 WODEN ACT 2606 AUSTRALIA E-mail address: pct@ipaustralia.gov.au Facsimile No. (02) 6285 3929	Authorized Officer JAMES DZIEDZIC Telephone No. (02) 6283 2495

I.	Basis of the report

1. With regard to the **elements** of the international application:*

   [X] the international application as originally filed.

   [ ] the description,   pages   ,   as originally filed,

                                  pages   ,   filed with the demand,

                                  pages   ,   received on   with the letter of   .

   [ ] the claims,   pages   ,   as originally filed,

                                  pages   ,   as amended (together with any statement) under Article 19,

                                  pages   ,   filed with the demand,

                                  pages   ,   received on   with the letter of   .

   [ ] the drawings,   pages   ,   as originally filed,

                                  pages   ,   filed with the demand,

                                  pages   ,   received on   with the letter of   .

   [ ] the sequence listing part of the description:

                                  pages   ,   as originally filed

                                  pages   ,   filed with the demand

                                  pages   ,   received on   with the letter of   .

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.
   These elements were available or furnished to this Authority in the following language   which is:

   [ ] the language of a translation furnished for the purposes of international search (under Rule 23.1(b)).

   [ ] the language of publication of the international application (under Rule 48.3(b)).

   [ ] the language of the translation furnished for the purposes of international preliminary examination (under Rules 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, was on the basis of the sequence listing:

   [ ] contained in the international application in written form.

   [ ] filed together with the international application in computer readable form.

   [ ] furnished subsequently to this Authority in written form.

   [ ] furnished subsequently to this Authority in computer readable form.

   [ ] The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

   [ ] The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

4. [ ] The amendments have resulted in the cancellation of:

   [ ] the description,   pages

   [ ] the claims,   Nos.

   [ ] the drawings,   sheets/fig

5. [ ] This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).**

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*   *Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17).*

**   *Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report*

V.	Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1.   Statement

Novelty (N)	Claims	**1-20**	**YES**
	Claims		**NO**
Inventive step (IS)	Claims	**1-20**	**YES**
	Claims		**NO**
Industrial applicability (IA)	Claims	**1-20**	**YES**
	Claims		**NO**

2.   Citations and explanations (Rule 70.7)

The invention relates to a method and apparatus for the removal and causticisation of sodium oxalate and/or sodium sulphate from a Bayer liquor containing sodium carbonate which includes the steps of removing aluminate ions from the liquor by forming a carbonate and/or sulphate bearing hydrocalumite, as defined on page 4 lines 19-22, and treating the liquor with lime to remove and causticise any residual carbonate ions and oxalate ions present. Documents cited in the search report are

i)   AU 20347/95 (Worsley)
ii)   AU 50778/93 (Worsley)
iii)   AU 32197/93 (Aluminium Pechiney)
iv)   AU 27000/92 (BHP)
v)   AU 35943/89 (Vereinigte Aluminium-Werke)
vi)   US 5888461 (Soirat)
vii)   US 5728180 (Williams)

Document i) discloses the removal of sodium sulphate and sodium oxalate from Bayer liquors. This is achieved by controlling the sodium aluminate concentration to inhibit dissolution of impurities.

Document ii) discloses the removal of oxalate from Bayer liquors by growing coarse clusters and/or spherulites of oxalate during aluminium hydroxide precipitation. These can be selectively removed and subsequently subjected to biological degradation.

Document iii) discloses the removal of oxalate from Bayer liquors by precipitating out oxalate using a destabilisation agent which affects the state of supersaturation of the oxalate. The agent can be lime.

Document iv) discloses removing impurities, eg oxalate, by oxidisation using manganese dioxide.

Document v) discloses removing oxalate from Bayer liquors by separating out aluminium hydroxide, removing a part of the spent lye, adding sodium oxalate crystals seed and crystallising out sodium oxalate.

Document vi) discloses removing oxalate from Bayer liquors by using a destabilisation agent as described for document iii) above.

Document vii) discloses oxalate removal from liquors where organic poisons in the oxalate solution are removed using two or more absorbents.

Supplemental Box

(To be used when the space in any of the preceding boxes is not sufficient)

Continuation of :Box V
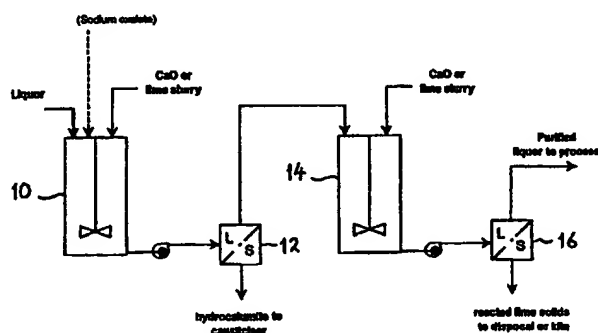
From the foregoing it is apparent that none of the cited documents discloses process steps which require aluminate ion separation from the liquor through the formation of a carbonate and/or sulphate bearing hydrocalumite which is then subsequently treated to remove and causticise oxalate ions. In view of this the invention is considered novel and inventive. It is also industrially applicable.

(51) International Patent Classification [7] : C01F 7/47, 7/06	**A1**	(11) International Publication Number: **WO 00/56660** (43) International Publication Date: 28 September 2000 (28.09.00)

(54) Title: PROCESS FOR THE REMOVAL OF OXALATE AND/OR SULPHATE FROM BAYER LIQUORS

(57) Abstract

A process for the removal and causticisation of sodium oxalate and/or sodium sulphate from a Bayer process liquor containing sodium carbonate and one or both of sodium oxalate and sodium sulphate in an alumina refinery is described. The process is based on the observation that to efficiently causticise sodium oxalate solutions, it is first necessary to remove the aluminate ion from solution, optionally with recovery of the aluminate ion in some later step. This is effected by removing aluminate ions from the Bayer liquor through the formation of a carbonate-bearing hydrocalumite and/or sulphate-bearing hydrocalumite. The liquor may then be treated with sufficient lime to remove and causticise any residual carbonate ions and some or all of the oxalate ions present so that any reacted lime solids thus formed can be separated and safely disposed of. The process may include a pre-causticisation step in which the Bayer liquor is first causticised to reduce the concentration of carbonate ions, prior to the step of removing aluminate ions. The invention provides an effective process for the removal of sodium sulphate and a practical method for the recovery of soda from sodium sulphate. The efficiency of lime utilisation can also be dramatically increased from about 20 % to 80 % (if sulphate removal is not the objective) wherein alumina losses can be minimised. The oxalate concentration of the process liquor is also substantially lower than can usually be achieved in processes based on sodium oxalate-crystallisation.

PROCESS FOR THE REMOVAL OF OXALATE AND/OR SULPHATE FROM BAYER LIQUORS

FIELD OF THE INVENTION

5 The present invention relates to a process and apparatus for the removal and causticisation of sodium oxalate and/or sodium sulphate from a Bayer process liquor.

BACKGROUND TO THE INVENTION

In the Bayer process for the production of alumina, bauxite is digested in a caustic liquor, 10 generally under conditions of elevated temperature and pressure. A variety of organic and inorganic impurities are invariably extracted at the same time, reacting with caustic soda to form their sodium salts. In addition, some of the organic compounds can undergo degradation, ultimately producing sodium carbonate and the sodium salts of a range of simple carboxylic acids. The formation of these impurities represents a major loss of 15 caustic from the refinery's liquor streams. This caustic must either be replaced, or recovered in some way from the impurities.

The recovery of caustic from sodium carbonate is a commonplace activity in most alumina refineries. The causticisation of sodium carbonate is generally effected by the addition of 20 lime, which reacts with the sodium carbonate to form calcium carbonate, thereby liberating sodium hydroxide. An improved version of this process is described in our co-pending International Application No. PCT/AU99/00757, filed on the 25th of September 1999 and entitled "Improved Bayer Causticisation". The contents of PCT/AU99/00757 are incorporated herein by reference.

25

Of the other impurities, sodium oxalate and sodium sulphate are among the most significant. The presence of sodium oxalate in Bayer process streams is problematical owing to its very limited solubility. This creates a number of well-known problems within the alumina refinery. Sodium sulphate is much more soluble, and can accumulate to very 30 high concentrations. This causes a different set of problems, particularly with respect to the refinery's productivity. The problems associated with this impurity in Bayer process liquors, and a process for its separation, have been described in Australian patent No. 673306.

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Many prior art processes have been described for the removal of sodium oxalate and sodium sulphate from Bayer liquors. Some of these processes remove both impurities concurrently. In most cases, these processes advocate that the impurity is discarded after removal from the liquor stream. However, a small number of the above processes also provide a means for the recovery of soda from sodium oxalate. None describe a practical method for the recovery of soda from sodium sulphate, requiring that it be discarded. However, disposal of sodium sulphate is not straightforward.

Environmental considerations preclude disposal of sodium sulphate into natural water systems, and since it is highly soluble, it must be disposed in a suitably lined or otherwise isolated sanitary landfill if it is not to enter groundwater systems. In the alumina refinery, disposal of sodium sulphate to the red mud residue disposal areas results in the eventual return of most of the sodium sulphate to the process liquor stream with the recovered lake water.

Whilst it is preferable to utilise the sodium sulphate in some way, for example by conversion into useful products, options for this are extremely limited. Electrolytic cells are commercially available which convert sodium sulphate into sodium hydroxide and either sodium bisulphate or sulphuric acid. However, these are generally restricted to reasonably pure solutions in which scales are unlikely to form, because the membranes used in the cells are sensitive to fouling. Other processes have been investigated including reductive processes such as the Leblanc process, and the Peniakoff process for production of gibbsite from bauxite. These latter processes are not currently practised, as they are inefficient, costly and produce environmentally unacceptable by-products.

Thus, there is a significant need for an economic process for the processing of sodium sulphate into more useful products, and/or for the immobilisation of the sulphate anion in an environmentally acceptable, insoluble material.

Most alumina refineries practice some form of oxalate removal process. In general, these processes are based on variations of the following two procedures:

1.   Sodium oxalate is permitted to coprecipitate with gibbsite in the refinery's gibbsite

precipitation circuit. The co-crystallised oxalate reports to the refinery's gibbsite seed preparation facility, where it is removed by washing with water or dilute liquor. The oxalate-rich washings are then further treated to remove oxalate either by seeding and evaporation to recrystallise sodium oxalate or, by reaction with lime, as calcium oxalate.

5

2.   Oxalate co-crystallisation is avoided by crystallising and removing sodium oxalate in a side-stream of one of the refinery's main process streams (usually a spent liquor stream). The side stream is evaporated to increase the supersaturation of the sodium oxalate and directed to a series of oxalate crystallisers where it is seeded with recycled sodium oxalate

10 crystals. After solid/liquid separation, the clarified and now oxalate-depleted liquor is returned to the process. A portion of the solid sodium oxalate is recycled to act as seed, while the remainder is either discarded or processed to recover soda. An example of this process is outlined in US 3,899,571.

15 Most processes for the recovery of the soda values from sodium oxalate are based on reactions with lime. In some processes, the separated sodium oxalate cake is first burnt in a kiln to produce sodium carbonate, which is subsequently causticised by reaction with lime. This process is costly to operate, and the conversion to sodium carbonate is not always complete.

20

In other processes, a solution rich in sodium oxalate, such as the washings from the seed circuit of a refinery that practices coprecipitation of oxalate, is directly reacted with lime to form calcium oxalate. However, whilst very low oxalate concentrations can be achieved in the treated stream in this way, the efficiency of lime utilisation is very poor, due to the

25 formation of calcium aluminates such as tricalcium aluminate (TCA), unless the stream is very low in caustic and sodium aluminate. Consequently, this process can only be applied to dilute liquors.

SUMMARY OF THE INVENTION

30 The present invention was developed with a view to providing a means for the direct removal of sodium sulphate or sodium oxalate, or combinations of both, in Bayer process liquors with the production of sodium hydroxide. The unwanted anion is isolated in an insoluble solid material that can be disposed of in a conventional sanitary landfill, thus

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preventing the return of the unwanted anions to the refinery via the refinery's lake system.

Throughout this specification, we have used conventional North American terminology for the description of Bayer solution compositions. Thus, 'C' refers to the caustic

5   concentration of the liquor, this being the sum of the sodium aluminate and sodium hydroxide content of the liquor expressed as equivalent g/L of sodium carbonate. 'S' refers to the sum of C and the true concentration of sodium carbonate. Thus, S-C gives the actual concentration of Na_2CO_3 in the liquor, in g/L. 'A' refers to the concentration of sodium aluminate in the liquor, expressed as equivalent g/L of Al_2O_3.

10

Sodium oxalate concentration is expressed as g/L of $Na_2C_2O_4$. Sodium sulphate concentration is expressed as g/L of Na_2SO_4. 'TS' refers to the sum of all sodium salts in solution, expressed as the equivalent concentration in g/L of sodium carbonate.

15   Lime refers either to calcium oxide, or more preferably, calcium hydroxide. Lime efficiency is defined as the percentage ratio of the number of moles of sodium hydroxide produced to the number of moles of lime consumed, divided by two.

The term Hydrocalumite is used to refer to any layered double hydroxide compound

20   formed between calcium and aluminium, within which charge balancing anions are intercalated. Typically, these compounds will be of the form $[Ca_2Al(OH)_6]_2 \cdot X \cdot nH_2O$, where 'X' represents a charge-balancing anion or anions.

Throughout this specification the term "comprising" is used inclusively, in the sense that

25   there may be other features and/or steps included in the invention not expressly defined or comprehended in the features or steps subsequently defined or described. What such other features and/or steps may include will be apparent from the specification read as a whole.

According to one aspect of the present invention there is provided a process for the

30   removal and causticisation of sodium oxalate and/or sodium sulphate from a Bayer process liquor containing sodium carbonate and one or both of sodium oxalate and sodium sulphate in an alumina refinery, the process comprising the steps of:

- 5 -

removing aluminate ions from the Bayer liquor through the formation of acarbonate-bearing hydrocalumite and/or sulphate-bearing hydrocalumite; and,

5   treating the liquor with sufficient lime to remove and causticise any residual carbonate ions and some or all of the oxalate ions present whereby any reacted lime solids thus formed can be separated and safely disposed of.

Preferably the process comprises a further step, prior to said step of removing aluminate ions, in which the liquor is enriched with sulphate and/or oxalate such that any aluminate

10   and/or carbonate ions entering with the sulphate and/or oxalate are also removed.

Preferably the process comprises a further step, following said step of removing aluminate ions, of separating the carbonate-bearing hydrocalumite and/or sulphate-bearing hydrocalumite from the Bayer liquor to form a clarified liquor.

15

In another embodiment the process further comprises a pre-causticisation step in which the Bayer liquor is first causticised to reduce the concentration of carbonate ions, prior to said step of removing aluminate ions. Typically said pre-causticisation step includes heating the liquor, adding sufficient lime to react with the carbonate ions to produce calcium

20   carbonate and separating the calcium carbonate from the liquor. Optionally the heated liquor is enriched with sulphate and/or oxalate prior to causticisation to ensure that any carbonate ions entering with the sulphate and/or oxalate are also causticised.

According to another aspect of the present invention there is provided an apparatus for the

25   removal and causticisation of sodium oxalate and/or sodium sulphate from a Bayer process liquor containing sodium carbonate and one or both of sodium oxalate and sodium sulphate in an alumina refinery, the apparatus comprising:

means for removing aluminate ions from the Bayer liquor through the formation of a

30   carbonate-bearing hydrocalumite and/or sulphate-bearing hydrocalumite; and,

means for treating the liquor with sufficient lime to remove and causticise any residual carbonate ions and some or all of the oxalate ions present whereby any

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reacted lime solids thus formed can be separated and safely disposed of.

In one embodiment said means for removing aluminate ions comprises a first reaction vessel to which sufficient lime is added to react with all of the aluminate ions in the liquor.
5 Preferably the apparatus of this embodiment further comprises a means for separating the carbonate-bearing hydrocalumite and/or sulphate-bearing hydrocalumite from the liquor to form a clarified liquor. Preferably the means for treating the liquor comprise a second reaction vessel to which sufficient lime is added to react with the sodium oxalate in the clarified liquor to form calcium oxalate and with any remaining carbonate ions to form
10 sodium carbonate.

In another embodiment said means for removing aluminate ions and said means for treating the liquor are comprised in a single reaction vessel to which sufficient lime is added to react with the aluminate ions to form said carbonate-bearing and/or sulphate-
15 bearing hydrocalumite, together with sufficient additional lime to react with the sodium oxalate to form calcium oxalate.

The inventors' theories on the chemical reactions in the process and apparatus of the present invention are merely examples of possible reactions thought to be taking place and
20 are not intended to be limiting in any way.

BRIEF DESCRIPTION OF DRAWINGS

In order to facilitate a better understanding of the nature of the invention preferred embodiments of the process and apparatus for the removal and causticisation of sodium
25 oxalate and/or sodium sulphate will now be described in detail, by way of example only, with reference to the accompanying drawings in which:

Figure 1 is a simplified process flow diagram for the causticisation of sodium oxalate in accordance with one embodiment of the present invention; and,

30

Figure 2 is a simplified process flow diagram for the causticisation and removal of sodium sulphate and sodium oxalate in accordance with another embodiment of the present invention.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

This invention is based upon the following two key findings:

1.   The inventors have found that lime will not react with sodium oxalate to form
5   calcium oxalate and sodium hydroxide in Bayer process liquors unless the
       concentration of sodium aluminate is close to zero.

2.   It is known that hydrocalumite-type structures are formed by the reaction of lime
      with sodium aluminate solutions such as Bayer liquors, and that these structures will
10   incorporate anions into the interlayer regions. The order of preference by which
       anions are incorporated is critical in the utilisation of this property. The inventors
       have found that the order of preference of anion incorporation in Bayer liquors is
       carbonate >sulphate > oxalate. This contrasts with published literature which
       indicates that the order is carbonate > oxalate > sulphate. ["Layered Double
15   Hydroxides for Treatment of Bayer Process Lake Water" AJ Perrotta, FS Williams
       and LC Stonehouse, Light Metals (1997), 37-48].

The above two findings explain why the conventional approaches to causticising sodium
oxalate in Bayer process solutions are so inefficient with respect to lime use, and must be
20 restricted to low S liquors. The addition of lime to these solutions results in the formation
of hydrocalumite (Hc). Since carbonate is usually present in these liquors, the Hc formed
is primarily the carbonate form:

$$4Ca(OH)_2 + 2Al(OH)_4^- + \frac{1}{2}CO_3^{2-} + nH_2O \leftrightarrow [Ca_2Al(OH)_6]_2 \cdot OH \cdot \frac{1}{2}CO_3 \cdot nH_2O + 3OH^- \qquad ...(1)$$
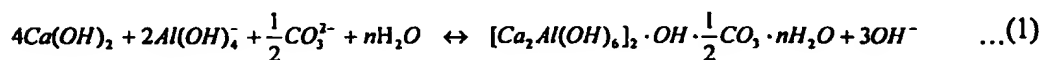
25

If sufficient lime has been added, this reaction will proceed until virtually all of the
aluminate ion in solution has been removed, other than a small equilibrium concentration.
Note that this is a very inefficient causticising reaction, in that eight moles of $Ca(OH)_2$ are
required to causticise one mole of Na_2CO_3.

30

Rarely, insufficient carbonate may be present in the liquor to counterbalance all of the Hc.

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In this case, if sulphate and/or oxalate are also present, sulphate is preferentially incorporated into the inter-layer regions of the hydrocalumite structure, as indicated by the following equation:

$$5 \quad 4Ca(OH)_2 + 2Al(OH)_4^- + SO_4^{2-} + nH_2O \leftrightarrow [Ca_2Al(OH)_6]_2SO_4 \cdot nH_2O + 4OH^- \qquad \ldots(2)$$
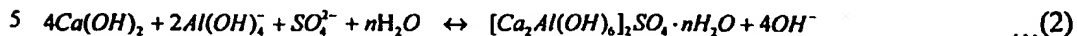
If insufficient sulphate is present to counterbalance all of the Hc formed, a small amount of oxalate can be incorporated into the Hc structure, as follows:

$$10 \quad 4Ca(OH)_2 + 2Al(OH)_4^- + C_2O_4^{2-} + nH_2O \leftrightarrow [Ca_2Al(OH)_6]_2C_2O_4 \cdot nH_2O + 4OH^- \qquad \ldots(3)$$

Once the aluminate has been reduced to close to its equilibrium concentration in contact with Hc, the addition of further lime will result in the following reaction:

$$15 \quad Ca(OH)_2 + C_2O_4^{2-} + H_2O \leftrightarrow CaC_2O_4 \cdot H_2O + 2OH^- \qquad \ldots(4)$$

Reaction (4) is preferred over reaction (3), since only one mole of calcium hydroxide is required to causticise each mole of oxalate, and no alumina is consumed.

20 The reasons for the poor lime efficiency of conventional sodium oxalate causticisation processes should be apparent from the above explanation to those skilled in the arts of the Bayer process. Most of the lime is consumed forming Hc according to equation (1) above. When the dissolved alumina has been consumed, any additional lime will react with the oxalate and residual carbonate to form calcium oxalate and calcium carbonate
25 respectively. Consequently, since most Bayer liquors contain substantial dissolved alumina, and the amount is usually proportional to the S concentration of the liquor, it is clear why the process is usually restricted to solutions of low S concentration.

From the preceding discussion, it is apparent that to efficiently causticise sodium oxalate
30 solutions, it is first necessary to remove the aluminate ion from solution, preferably with recovery of the aluminate ion in some later step. In this invention, this removal is effected

by reacting the aluminate with lime in such a manner that productive use is made of the hydrocalumite so formed. In its preferred form the process consists of the following basic steps:

1. Removal of carbonate ions from a Bayer liquor containing sodium carbonate and one or both of sodium oxalate and sodium sulphate, either through the formation of calcium carbonate using any suitable carbonate causticisation process known to those skilled in the arts of the Bayer process, or through the formation of carbonate-bearing hydrocalumite according to equation (1) above.

2. Separation and disposal of any calcium carbonate formed in Step (1) above, or separation and recovery of any carbonate-bearing hydrocalumite formed in Step (1). The recovered Hc may then be used for further causticisation, using the process described in co-pending International Application No. PCT/AU99/00757, thereby recovering the alumina consumed in Step (1).

3. Treatment of the clarified liquor produced in Step (2) with sufficient lime to remove any dissolved alumina remaining after Step (1), plus enough additional lime to react any remaining sodium carbonate and the sodium oxalate. This results in the following sequence of reactions:

   the removal and causticisation of some or all of the residual carbonate as carbonate-bearing Hc according to equation (1);

   the removal and causticisation of some or all of the sodium sulphate as sulphate-bearing Hc according to equation (2), and;

   the removal and causticisation of sodium oxalate as predominantly calcium oxalate monohydrate according to equation (4). Some calcium carbonate may also form.

4. Separation and disposal of the reacted lime solids formed in Step (3), and return of the clarified caustic solution to a suitable location within the Refinery.

The process of the invention for the causticisation and removal of sodium oxalate and/or sodium sulphate is further described and illustrated in the following two examples. These examples are illustrative of a variety of possible implementations and are not to be construed as limiting the invention in any way.

5

EXAMPLE 1

In this example, oxalate is causticised to sodium hydroxide with high lime efficiency and with little loss of alumina. The process may be operated in either batch or continuous mode with suitable selection of equipment.

10

Referring to the simplified process flow diagram of Figure 1, a Bayer process liquor of S concentration of between 0 and 250 g/L, preferably less than 150 g/L is directed into a reaction vessel 10 and maintained at a temperature of between 20 and 90°C, preferably between 50 and 70°C. The type of reactor is not critical, for example a CSTR may be

15 used, provided that sufficient agitation is applied to ensure that all of the solids are adequately suspended. If the solution is not already enriched with oxalate, sodium oxalate in either solid form or as an aqueous solution may optionally be added, provided that the solubility of sodium oxalate is not exceeded after mixing with the liquor to be treated. A suitable stream for treatment would be the filtrate from the gibbsite seed washing facility

20 in a refinery practising oxalate co-precipitation. Alternatively, a suitable stream could be prepared by dissolving oxalate cake in a dilute liquor such as the filtrate from the product washing filters.

Sufficient lime (preferably slaked lime) is added to the reaction vessel to react with

25 substantially all of the dissolved alumina in the solution, forming a carbonate-bearing hydrocalumite. The lime requirement can be calculated using equation (1) above. The residence time in this reactor is not critical. The reaction is generally found to be complete in less than five minutes, but residence times of up to 2 hours have little or no adverse effect. The preferred residence time is 30 minutes. Excessive residence times may result in

30 the undesirable formation of TCA, especially at high temperatures, causing a loss of efficiency.

The hydrocalumite solids and liquor are then separated using any suitable solid/liquid separation device 12 (preferably a pressure filter). The solids may then be used to causticise another liquor stream within the refinery, using the process revealed in co-pending International Application No. PCT/AU99/00757.

The clarified liquor is then directed to a second reaction vessel 14 and sufficient lime (preferably slaked lime) is added to react with the sodium oxalate to form calcium oxalate, and with any remaining sodium carbonate to form calcium carbonate. The amount of lime required may be calculated using equation (4) above, together with the following equation:

$$Ca(OH)_2 + CO_3^{2-} \leftrightarrow CaCO_3 + 2OH^- \qquad \ldots(5)$$

This reaction should be conducted between 20 and 140°C, preferably between 50 and 80°C, with a reaction time of between 15 mins and 4 hours, preferably 60 minutes.

The resultant slurry is then forwarded to any suitable solid/liquid separation device 16, preferably a pressure filter. The solids may be discharged to the alumina refinery's red mud disposal area, or after washing and drying, calcined for re-use.

Laboratory Test Results

STAGE 1 (a) - Removal of Aluminate Ions:

A calcium hydroxide slurry was prepared by slaking 31.3g of freshly calcined LR grade CaO in 350 mL of deionised water. 860 mL of simulated seedwash filtrate liquor was transferred to a 2 litre stainless steel Parr autoclave and heated to 60°C. The temperature was maintained thermostatically. Agitation was applied using a pitched blade turbine impeller rotating at 200 rpm. When the temperature of the system had equilibrated, the slaked lime slurry was added quantitatively.

Samples of the liquors were collected from the reactor and filtered using 0.45μm Acrodisc filters, at the commencement of the test and after 10 minutes of reaction.

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After 10 minutes of reaction, the agitator was stopped, the slurry removed from the autoclave and filtered under vacuum through a Whatmans #1 filter. This step was performed rapidly to avoid carbonation of the liquor by reaction with carbon dioxide in the air.

STAGE 1(b) - Use of Hydrocalumite for Causticisation:

The hydrocalumite solids (341g) collected by the filter were washed and air-dried. A sample of liquor was collected from the refinery mud washing circuit and filtered through a Whatman's #1 filter paper. 1000 mL of this liquor was placed in the autoclave and heated to 100°C. The temperature was maintained thermostatically. Agitation was applied using a pitched blade turbine impeller rotating at 200 rpm. When the temperature of the system had equilibrated, 80.4 g of the hydrocalumite solids was added quantitatively. The reaction was allowed to proceed for two hours with periodic sampling throughout.

STAGE 2 - Oxalate Removal

A portion of the filtrate (670 mL) from Stage 1(a) was returned to the autoclave and equilibrated at a temperature of 60°C. The agitator was restarted and operated at 200 rpm. Calcium hydroxide slurry, prepared by slaking 6.2g of freshly calcined LR grade CaO in 70 mL of deionised water, was then quantitatively added to the reactor.

Samples of the liquors were collected from the reactor and filtered using $0.45_{\mu}m$ Acrodisc filters, just prior to addition of the lime slurry and after 30 minutes of reaction. At 30 minutes, the agitator was stopped, the slurry removed from the autoclave and filtered under vacuum through a Whatmans #1 filter paper. As before, this step was performed rapidly to avoid carbonation of the liquor by carbon dioxide in air.

Comparison With Prior Art

To compare the efficiency of the proposed process with the prior art processes, a sample of the preceding liquor was reacted in a single stage process with slaked lime.

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A sample of the simulated seed-wash filtrate liquor above (900mL) was transferred to a 2 litre stainless steel Parr autoclave and heated to 60°C. Calcium hydroxide slurry was prepared by slaking 52.9g of freshly calcined LR grade CaO in 550 mL of deionised water. The temperature was maintained thermostatically. Agitation was applied using a

5   pitched blade turbine impeller rotating at 200 rpm. When the temperature of the system had equilibrated, the slaked lime slurry was added quantitatively.

Samples of the liquors were collected from the reactor and filtered using 0.45μm Acrodisc filters, at the commencement of the test and after 30 minutes of reaction.

10 After 30 minutes of reaction, the agitator was stopped, the slurry removed from the autoclave and filtered under vacuum through a Whatmans #1 filter. This step was performed rapidly to avoid carbonation of the liquor by reaction with carbon dioxide in the air.

15 Results:

Table 1: Liquor Analyses for Stage 1A of process.

Sample	Liquor Volume	A (g/L)	C (g/L)	S (g/L)	A/C	C/S	Na$_2$CO$_3$ (g/L)	NaCl (g/L)	Na$_2$SO$_4$ (g/L)	Na$_2$C$_2$O$_4$ (g/L)	TS (g/L)
Seedwash filtrate (t=0)	860 mL	19.8	55.6	66.4	0.356	0.837	10.8	5.4	15.1	8.8	89.8
t = 10 mins	1197 mL	2.8	51.6	52.3	0.054	0.987	0.7	3.4	8.2	5.3	64.5

Analysis of the solids by XRD indicated predominantly carbonate-bearing

20 hydrocalumite phases (major), some sulphate-bearing hydrocalumite (minor), a small amount of calcium oxalate (minor) and calcium carbonate (trace).

Table 2: Liquor Analyses for Stage 1B of process.

Sample	Liquor Volume	A (g/L)	C (g/L)	S (g/L)	A/C	C/S	Na$_2$CO$_3$ (g/L)	NaCl (g/L)	Na$_2$SO$_4$ (g/L)	Na$_2$C$_2$O$_4$ (g/L)	TS (g/L)
Mud Washer overflow (t=0)	1000 mL	66.5	103.9	126.7	0.640	0.820	22.8	9.0	24.2	1.8	174.3
t = 120 mins	1024 mL	68.0	109.9	123.8	0.619	0.888	13.9	9.0	24.3	2.5	170.2

Analysis of the solids by XRD indicated predominantly calcium carbonate (major
phase) with some carbonate-bearing hydrocalumite (trace).

As can be seen from the results in the above two tables, sodium carbonate has been
efficiently removed and caustic generated. Small amounts of sodium sulphate and

5 sodium oxalate have also been causticised.

Table 3: Liquor Analyses for 2nd stage of process

Sample	Liquor Volume	A (g/L)	C (g/L)	S (g/L)	A/C	C/S	Na$_2$CO$_3$ (g/L)	NaCl (g/L)	Na$_2$SO$_4$ (g/L)	Na$_2$C$_2$O$_4$ (g/L)	TS (g/L)
Seedwash filtrate (t=0)	670 mL	3.1	51.6	52.4	0.060	0.985	0.8	3.4	8.3	5.2	65.6
t = 30 mins	753 mL	0.3	51.3	51.8	0.006	0.990	0.5	2.6	4.5	1.5	58.4

10

Analysis of the solids by XRD indicated sulphate-bearing hydrocalumite
(major), calcium oxalate (major) and unreacted lime (trace).

It can be seen from the above results that the concentration of oxalate and

15 sulphate are greatly reduced. Small amounts of carbonate and other impurities
have also been removed.

Prior Art Process

20   Table 4: Liquor Analyses for Prior Art simulation.

Sample	Liquor Volume	A (g/L)	C (g/L)	S (g/L)	A/C	C/S	Na$_2$CO$_3$ (g/L)	NaCl (g/L)	Na$_2$SO$_4$ (g/L)	Na$_2$C$_2$O$_4$ (g/L)	TS (g/L)
Seedwash filtrate (t=0)	800 mL	20.0	55.2	66.1	0.362	0.835	10.9	4.9	14.9	10.10	89.1
t = 30 mins	1387 mL	0.2	51.8	52.4	0.004	0.989	0.6	2.8	5.1	0.9	57.8

Analysis of the solids by XRD indicated multiple hydrocalumite phases (due to

25 the presence of several different counterbalancing ions), calcium oxalate (major)

- 15 -

and some unreacted lime (trace).

Comparison of Example 1 with Prior Art

After due allowance for volumetric changes due to the input of water with slaked

5   lime, evaporative losses and changes in liquor composition, the following

performance results were obtained for Stages 1 and 2 of Example 1, and for the

simulation of the Prior Art process.

Table 5: Comparison of Causticisation and Removal

10   for Example 1 with Prior Art Process.

	Stage 1 t/t CaO	Stage 2 t/t CaO	Prior Art t/t CaO
Alumina loss (as Al_2O_3)	0	-0.298	-0.335
Sodium carbonate converted	-1.491	-0.026	-0.170
Sodium sulphate converted	-0.003	-0.351	-0.120
Sodium oxalate converted	0	-0.379	-0.148
Sodium chloride converted	0	-0.052	-0.009
Sodium hydroxide produced	1.269	0.492	0.317
Lime efficiency	88.9%	34.4%	22.2%

The average lime efficiency for Example 1 over both stages of the process was

77.9%.

15

It can be seen from the above results that the proposed process is considerably more

efficient in terms of its lime utilisation, and that far greater removal of both oxalate and

sulphate is effected per tonne of lime. Furthermore, it should be noted that the mass of

alumina lost per tonne of sodium oxalate removed is reduced by a factor of three.

EXAMPLE 2

In this example, sodium carbonate, sodium sulphate and sodium oxalate may all be
5   causticised and removed from solution. In essence, the process sacrifices dissolved
alumina for the recovery of the soda values of the sodium sulphate. Consequently, loss
of alumina is of the same magnitude as would have occurred in the prior art oxalate
causticisation processes, but with far greater recovery of caustic soda. While recovery
of the alumina is feasible, it cannot be done without attendant release of the sulphate,
10 and is hence not discussed here.

The principles of this variant of the process are best described by reference to the
simplified flow diagram shown in Figure 2. The process may be operated in either
batch or continuous mode with suitable selection of equipment.

15

A Bayer process liquor of S concentration of between 0 and 250 g/L, preferably less
than 150 g/L is first causticised to reduce the carbonate concentration, using any
suitable procedure known to those practised in the arts of the Bayer process.
Preferably, the process disclosed in co-pending International Application No.
20 PCT/AU99/00757 is used for this function, as this will ensure highest efficiency. In the
example given here, the liquor is heated to close to the atmospheric boiling point of the
liquor (approximately 100°C) by passing it through a heat exchanger 18 and directed
into a reaction vessel 20. The type of reactor is not critical. For example, a CSTR may
be used, provided that sufficient agitation is applied to ensure that all of the solids are
25 adequately suspended.

If the solution is not already enriched with sulphate and/or oxalate, these may be added
into this tank. Sodium oxalate may be added in either solid form or as an aqueous
solution, provided that the solubility of sodium oxalate is not exceeded. The sodium
30 sulphate can be prepared using any of the techniques described earlier and added either
in solid form or as an aqueous solution, once again ensuring that the solubility of

anhydrous sodium sulphate is not exceeded. For example, a liquor stream fortified with sulphate suitable for treatment by this process is produced using the process described in Australian patent No. 673306.

5   While it is feasible to add these impurities into the second tank, or other suitable location, it is preferable if this is done in the first tank, or in the liquor stream prior to entering the first tank. This is to ensure that any sodium carbonate entering with the oxalate or sulphate is causticised, otherwise efficiency may be degraded.

10 Sufficient lime (preferably slaked lime) is added to the reaction vessel 20 to react with the sodium carbonate: the amount will depend upon the liquor composition and the causticisation technique employed. However, care should be taken to avoid overcharging of lime, as this will reduce the lime efficiency of the process. In the example given here, a residence time of approximately 1 hour was sufficient to ensure
15 optimum causticisation.

The slurry is then discharged to a solid/liquid separation device 22, which may be of any suitable design (preferably a pressure filter). The solids, which will consist primarily of calcium carbonate, may be discarded. Alternatively the solids may be
20 further washed to recover soda, and then calcined for re-use.

The clarified liquor is cooled to between 30 and 90∘C, preferably between 50∘C and 70∘C in a heat exchanger 24 and directed to a second reaction vessel 26. The heat exchanger 24 may be located before solid liquid separation device 22 to make the
25 operating conditions within the solid/liquid separation device less aggressive. This will allow for a greater selection of solid/liquid separation devices. Once the liquid is separated and cooled, sufficient lime (preferably slaked lime) is added to react with the alumina, forming hydrocalumite, together with sufficient additional lime to react with the sodium oxalate to form calcium oxalate. The Hc thus formed will consist of a
30 mixture of both carbonate and sulphate-bearing species, depending upon the amount of residual carbonate remaining in the liquor. The carbonate-bearing species will form

- 18 -

preferentially, according to equation (1), followed by the sulphate-bearing species according to equation (2).

Thus, the ability of this process to causticise sodium sulphate will depend strongly on the efficiency of the pre-causticisation step in Tank 20, as well as the dissolved alumina content of the liquor, assuming that sodium sulphate is present in excess. Sodium oxalate will be causticised according to equation (4). The lime charge required can therefore be calculated on the basis of the liquor composition and the above three equations. To ensure efficient removal of the sodium oxalate, a slight excess of lime above the calculated amount (approximately 10%) is advisable.

The residence time required in the reactor 26 is between 30 minutes and 4 hours, preferably approximately 2 hours. Shorter residence times may be used if oxalate removal is not of paramount importance – in this case, the lime charge may be decreased accordingly.

The discharge from the tank 26 is pumped to a solid/liquid separation unit 28 such as a filter, centrifuge, or gravity separation device. The solids may then be disposed directly, or further washed and filtered before disposal. The washings can be returned to the second reactor, or mixed with the clarified liquor.

The clarified liquor, which will consist primarily of sodium hydroxide, may be returned to a suitable location within the refinery.

Laboratory Test Results

STAGE 1:

A calcium hydroxide slurry was prepared by slaking 5.65g of freshly calcined LR grade CaO in 60 ml of deionised water. Refinery seed-wash filtrate liquor was collected and filtered through a Whatmans #1 filter paper. 1000mL of this filtered liquor was transferred to a 2 litre stainless steel Parr autoclave and heated to 100°C. The temperature was maintained thermostatically. Agitation was applied using a pitched

blade turbine impeller rotating at 200 rpm. When the temperature of the system had equilibrated, the slaked lime slurry was added quantitatively.

Samples of the liquor were collected from the reactor and filtered using $0.45_{\mu}m$
5 Acrodisc filters, at the commencement of the test and after 60 minutes of reaction.

After 60 minutes of reaction, the agitator was stopped, the slurry removed from the autoclave and filtered under vacuum through a Whatmans #1 filter. This step was performed rapidly to avoid carbonation of the liquor by reaction with carbon dioxide in
10 the air. The results of analysis of the liquor following Stage 1 are given below in Table 6.

Table 6: Liquor Analyses for 1ˢᵗ stage of process.

Sample	Liquor Volume	A (g/L)	C (g/L)	S (g/L)	A/C	C/S	Na₂CO₃ (g/L)	NaCl (g/L)	Na₂SO₄ (g/L)	Na₂C₂O₄ (g/L)	TS (g/L)
Seedwash filtrate (t=0)	1000	20.0	55.2	66.1	0.362	0.835	10.9	5.1	14.9	10.1	89.1
t=60 mins	1053	18.8	61.2	63.7	0.307	0.961	2.5	4.9	14.1	9.4	84.6

15

Analysis of the solids by XRD indicated predominantly calcium carbonate (major phase) with some carbonate-bearing hydrocalumite (minor phase).

STAGE 2:

20 The filtrate (860 mL) was returned to the autoclave and equilibrated at a temperature of 60°C. The agitator was restarted and operated at 200 rpm. A calcium hydroxide slurry prepared by slaking 44.2g of freshly calcined LR grade CaO in 450 mL of deionised water was then quantitatively added to the reactor.

25 Samples of the liquors were collected from the reactor and filtered using $0.45_{\mu}m$ Acrodisc filters, just prior to addition of the lime slurry and after 2 hours of reaction. At two hours, the agitator was stopped, the slurry removed from the autoclave and filtered under vacuum

- 20 -

through a Whatmans #1 filter paper. As before, this step was performed rapidly to avoid carbonation of the liquor by carbon dioxide in air. The results of analysis of the liquor following Stage 2 of the process are given in Table 7 below.

5 　　　　　　　　　　Table 7: Liquor Analyses for 2nd stage of process

Sample	Liquor Volume	A (g/L)	C (g/L)	S (g/L)	A/C	C/S	Na_2CO_3 (g/L)	NaCl (g/L)	Na_2SO_4 (g/L)	$Na_2C_2O_4$ (g/L)	TS (g/L)
Seedwash filtrate (t=0)	860	19.5	63.5	65.9	0.306	0.933	2.4	4.9	15.0	10.0	89.0
t=60 mins	1293	0.8	56.1	55.6	0.012	0.993	0.5	2.6	0.8	1.4	59.2

Analysis of the solids by XRD indicated multiple hydrocalumite phases (due to the presence of several different counterbalancing anions) as the major component, calcium oxalate (major phase) and unreacted lime (trace).

10

It can be seen from the above results that the concentrations of carbonate, oxalate and sulphate are greatly reduced, and that the C/S ratio has increased. Some reduction in sodium chloride concentration has also occurred, although the reduction is minor. Similarly, a mass balance over soda indicates that small quantities of impurities other than

15 those analysed here have also been causticised and removed.

After due allowance for volumetric changes due to the input of water with slaked lime, evaporative losses and changes in liquor composition, the following performance results were calculated per tonne of CaO consumed:

20

25

Table 8: Causticisation and Removal Performance for Example 2 compared with Prior
Art Process

	Example 2 t/t CaO	Prior Art t/t CaO
Alumina loss (as Al_2O_3)	-0.326	-0.335
Sodium carbonate converted	-0.167	-0.170
Sodium sulphate converted	-0.244	-0.120
Sodium oxalate converted	-0.142	-0.148
Sodium chloride converted	-0.016	-0.009
Sodium hydroxide produced	0.394	0.317
Total lime efficiency	27.6%	22.2%

From the above description of several preferred embodiments and illustrative examples, it
will be apparent that the process and apparatus for removal and causticisation of sodium
oxalate and/or sodium sulphate has a number of advantages, including the following:

(i)   it provides an effective process for the removal of sodium sulphate;

(ii)   for the first time it provides a practical method for the recovery of soda from sodium
        sulphate;

(iii)   the efficiency of lime utilisation can be dramatically increased from about 20% to
        80% (if sulphate removal is not the objective);

(iv)   the oxalate concentration of the processed liquor is substantially lower than can
        usually be achieved in processes based on sodium oxalate crystallisation;

(v)   the efficiency of lime utilisation is greater than prior art processes based on reactions
        of lime with oxalate-rich Bayer liquors;

(vii)   unlike oxalate removal processes based on sodium oxalate crystallisation, the
        process is not appreciably affected by the presence of organic poisons. This obviates
        the need for special organic poison removal processes, and contributes to consistent
        oxalate removal;

(viii) the process does not require the recycling of seed crystals and the associated equipment to achieve this;

(ix) the process does not require the use of strong liquors, raw caustic solutions or evaporation to supersaturate sodium oxalate. This simplifies oxalate removal and contributes to improved consistency of oxalate removal;

(x) unlike many prior art oxalate removal processes based on sodium oxalate crystallisation, the precipitated solids are consistent in their filtration and deliquoring characteristics, despite quite wide variations in solution composition. Liquor throughput and residual cake moisture can both be optimised; and,

(xi) the process provides supplementary causticisation capacity, raising the C/S of the refinery's liquors.

Numerous variations and modifications to the process and apparatus will suggest themselves to persons skilled in the Bayer process arts in Alumina refineries, in addition to those already described, without departing from the basic inventive concepts. All such variations and modifications are to be considered within the scope of the present invention, the nature of which is to be determined from the foregoing description and the appended claims.

THE CLAIMS DEFINING THE INVENTION

1. A process for the removal and causticisation of sodium oxalate and/or sodium sulphate from a Bayer process liquor containing sodium carbonate and one or both of sodium oxalate and sodium sulphate in an alumina refinery, the process comprising the steps of:

    removing aluminate ions from the Bayer liquor through the formation of a carbonate-bearing hydrocalumite and/or sulphate-bearing hydrocalumite; and,

    treating the liquor with sufficient lime to remove and causticise any residual carbonate ions and some or all of the oxalate ions present whereby any reacted lime solids thus formed can be separated and safely disposed of.

2. A process for the removal and causticisation of sodium oxalate and/or sodium sulphate as defined in claim 1, wherein the process comprises a further step, prior to said step of removing aluminate ions, in which the liquor is enriched with sulphate and/or oxalate such that any aluminate and/or carbonate ions entering with the sulphate and/or oxalate are also removed.

3. A process for the removal and causticisation of sodium oxalate and/or sodium sulphate as defined in claim 1, wherein the process comprises a further step, following said step of removing aluminate ions, of separating the carbonate-bearing hydrocalumite species and/or sulphate-bearing hydrocalumite species from the Bayer liquor to form a clarified liquor.

4. A process for the removal and causticisation of sodium oxalate and/or sodium sulphate as defined in claim 3, wherein the process comprises the further step of re-using said hydrocalumite species in an external causticisation process, whereby the aluminate contained within the hydrocalumite species is recovered.

5. A process for the removal and causticisation of sodium oxalate and/or sodium sulphate as defined in claim 1, wherein the process further comprises a pre-

causticisation step in which the Bayer liquor is first causticised to reduce the concentration of carbonate ions, prior to said step of removing aluminate ions.

6.   A process for the removal and causticisation of sodium oxalate and/or sodium sulphate as defined in claim 5, wherein said pre-causticisation step includes heating the liquor to close to boiling point, adding sufficient lime to react with the carbonate ions to produce substantially calcium carbonate and separating the reacted lime solids from the liquor.

7.   A process for the removal and causticisation of sodium oxalate and/or sodium sulphate as defined in claim 6, wherein the heated liquor is enriched with sulphate and/or oxalate prior to pre-causticisation to ensure that any carbonate ions entering with the sulphate and/or oxalate are also causticised.

8.   A process for the removal and causticisation of sodium oxalate and/or sodium sulphate as defined in claim 1, wherein the S concentration of the Bayer process liquor prior to the said step of removing aluminate ions is between 0 and 250g/l, and the liquor is maintained at a temperature of between 20°C and 90°C, with a reaction time of up to 120 minutes.

9.   A process for the removal and causticisation of sodium oxalate and/or sodium sulphate as defined in claim 8, wherein the S concentration of the Bayer process liquor prior to the said step of removing aluminate ions is less than 150 g/l, and the liquor is maintained at a temperature of between 50°C and 70°C, with a reaction time of approximately 30 minutes.

10.   A process for the removal and causticisation of sodium oxalate and/or sodium sulphate as defined in claim 9, wherein said step of treating the clarified liquor with sufficient lime is conducted at a temperature between 20°C and 140°C, with a reaction time of between 0.25 to 4.0 hours.

11.   A process for the removal and causticisation of sodium oxalate and/or sodium sulphate as defined in claim 10, wherein said step of treating the clarified liquor with
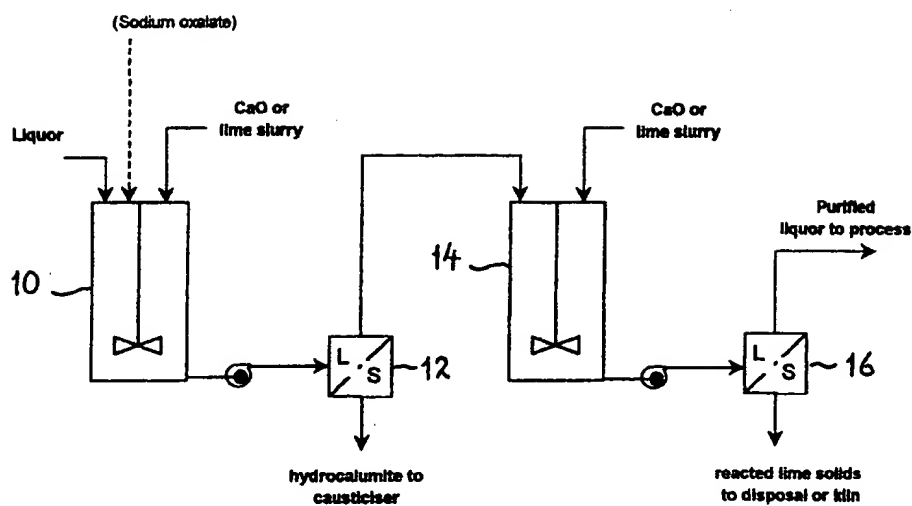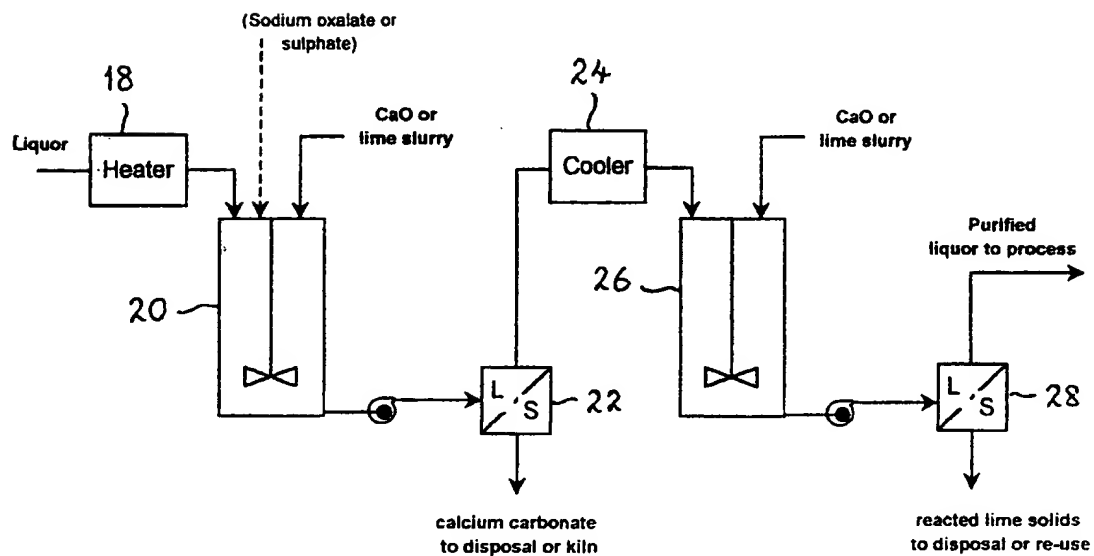
sufficient lime is conducted at a temperature between 50∘C and 80∘C, with a reaction time of between 0.5 to 1.0 hours.

12. A process for the removal and causticisation of sodium oxalate and/or sodium sulphate as defined in claim 11, wherein the said step of treating the liquor with sufficient lime is followed by a step of separating the reacted lime solids from the liquor and disposing of the solids or washing and drying the solids for calcination and re-use.

13. A process for the removal and causticisation of sodium oxalate and/or sodium sulphate as defined in claim 7, wherein the S concentration of the Bayer process liquor prior to said pre-causticisation step is between 0 and 250 g/l, and during said pre-causticisation step the liquor is heated to approximately 100∘C.

14. A process for the removal and causticisation of sodium oxalate and/or sodium sulphate as defined in claim 13, wherein the clarified liquor is cooled to between 30∘C and 90∘C prior to said step of removing the aluminate ions.

15. An apparatus for the removal and causticisation of sodium oxalate and/or sodium sulphate from a Bayer process liquor containing sodium carbonate and one or both of sodium oxalate and sodium sulphate in an alumina refinery, the apparatus comprising:

means for removing aluminate ions from the Bayer liquor through the formation of a carbonate-bearing hydrocalumite and/or sulphate-bearing hydrocalumite; and,

means for treating the liquor with sufficient lime to remove and causticise any residual carbonate ions and some or all of the oxalate ions present whereby any reacted lime solids thus formed can be separated and safely disposed of.

16. An apparatus for removal and causticisation of sodium oxalate and/or sodium sulphate as defined in claim 15, wherein said means for removing aluminate ions comprises a first reaction vessel to which sufficient lime is added to react with all of

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the aluminate ions in the liquor.

17.   An apparatus for removal and causticisation of sodium oxalate and/or sodium sulphate as defined in claim 16, wherein the apparatus further comprises a means for separating the carbonate-bearing hydrocalumite and/or sulphate-bearing hydrocalumite from the liquor to form a clarified liquor.

18.   An apparatus for removal and causticisation of sodium oxalate and/or sodium sulphate as defined in claim 17, wherein the means for treating the liquor comprises a second reaction vessel to which sufficient lime is added to react with the sodium oxalate in the clarified liquor to form calcium oxalate and with any remaining carbonate ions to form sodium carbonate.

19.   An apparatus for removal and causticisation of sodium oxalate and/or sodium sulphate as defined in claim 15, wherein said means for removing aluminate ions and said means for treating the liquor are comprised in a single reaction vessel to which sufficient lime is added to react with the aluminate ions to form said carbonate-bearing and/or sulphate-bearing hydrocalumite, together with sufficient additional lime to react with the sodium oxalate to form calcium oxalate.

20.   An apparatus for removal and causticisation of sodium oxalate and/or sodium sulphate as defined in claim 19, wherein another first reaction vessel is provided for treating the liquor, prior to entry into said single reaction vessel, with sufficient lime to react with the sodium carbonate and then discharged to a solid/liquid separation device for separating any solids, which will consist primarily of calcium carbonate, to form a clarified liquor.

1/1

(Sodium oxalate)

Liquor

CaO or
lime slurry

CaO or
lime slurry

Purified
liquor to process

10

14

12
L / S

16
L / S

hydrocalumite to
causticiser

reacted lime solids
to disposal or kiln

FIG.1.

(Sodium oxalate or
sulphate)

18

Liquor

Heater

CaO or
lime slurry

24

Cooler

CaO or
lime slurry

Purified
liquor to process

20

26

22
L / S

28
L / S

calcium carbonate
to disposal or kiln

reacted lime solids
to disposal or re-use

FIG.2.

INTERNATIONAL SEARCH REPORT

A.	CLASSIFICATION OF SUBJECT MATTER

Int. Cl. [7]: C01F 7/47, 7/06

According to International Patent Classification (IPC) or to both national classification and IPC

B.	FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C01F 7/04, 7/06, 7/46, 7/47

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

AU : IPC AS ABOVE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPAT, JAPIO, US(FULLTEXT)

C.	DOCUMENTS CONSIDERED TO BE RELEVANT	
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	AU 20347/95 A (Worsley Alumina) 8 February 1996	
A	AU 50778/93 A (Worsley Alumina) 2 June 1994	
A	AU 32197/93 A (Aluminium Pechiney) 12 August 1993	

[X] Further documents are listed in the continuation of Box C	[X] See patent family annex

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E"	earlier application or patent but published on or after the international filing date		
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means	"&"	document member of the same patent family
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search	Date of mailing of the international search report
15 May 2000	2 4 MAY 2000

Name and mailing address of the ISA/AU	Authorized officer
AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA E-mail address: pct@ipaustralia.gov.au Facsimile No. (02) 6285 3929	James Dziedzic Telephone No : (02) 6283 2495

Form PCT/ISA/210 (second sheet) (July 1998)

C (Continuation).	DOCUMENTS CONSIDERED TO BE RELEVANT	
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	AU 27000/92 A (Broken Hill Proprietary) 22 April 1993	
A	AU 35943/89 A (Vereinigte Aluminium-Werke AG) 7 December 1989	
A	US 5888461 A (Soirat) 30 March 1999	
A	US 5728180 A (Williams) 17 March 1998	

This Annex lists the known "A" publication level patent family members relating t the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in n way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member						
US	5888461	BR	9606529	CA	2199059	EP	782544	
		FR	2736908	AU	66179/96	WO	9703924	
AU	35943/89	EP	345654	US	4999170			
AU	32197/93	BR	9300494	CN	1076427	EP	555163	
		FR	2686872	HR	930104	WO	9606193	

END OF ANNEX

(51) International Patent Classification 6 : **C01F 7/06**	**A1**	(11) International Publication Number: **WO 00/18684**
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Published
With international search report.

(54) Title: IMPROVED BAYER CAUSTICISATION
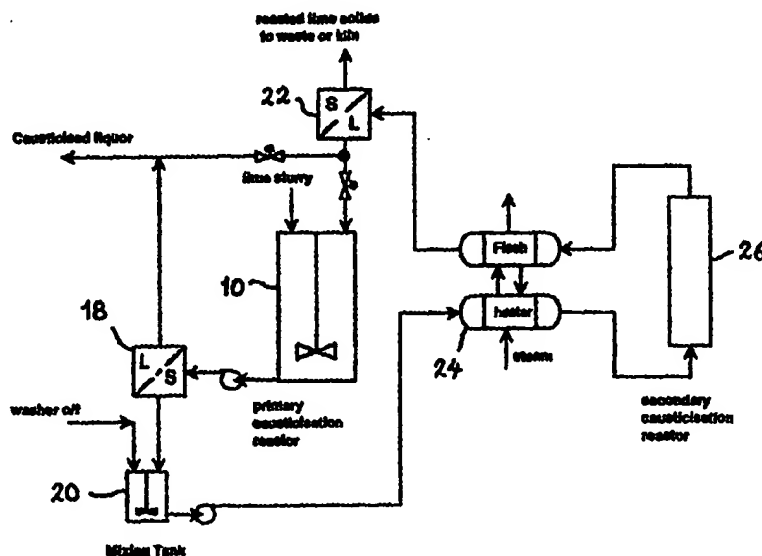
(57) Abstract

An improved process for the causticisation of Bayer liquors in an alumina refinery, the process including the steps of reacting lime with aluminate ions in a Bayer liquor within a primary reactor under controlled conditions of low to moderate temperature (between 70–80 °C) and agitation, to form substantially only a hydrocalumite species and hydroxyl ions; and a secondary reactor wherein said hydrocalumite species formed is subjected to heating in contact with a Bayer liquor under controlled conditions so as to cause the hydrocalumite species to react with the liquor to form calcium carbonate, aluminate ions and hydroxyl ions, whereby a causticised Bayer liquor is obtained and wherein the efficiency of lime utilisation is substantially increased and/or alumina losses are minimised.

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IMPROVED BAYER CAUSTICISATION

FIELD OF THE INVENTION

The present invention relates to an improved process and apparatus for the causticisation of

5   Bayer liquors in an alumina refinery and relates particularly, though not exclusively, to a process in which the achievable C/S ratio is significantly increased and/or in which substantially improved lime utilisation efficiencies and/or reduced alumina losses can be achieved.

BACKGROUND TO THE INVENTION

10   In the Bayer process for alumina production, a concentrated sodium aluminate solution is produced by grinding and digesting bauxite in a caustic solution, usually under conditions of elevated temperature and pressure. After clarification of the slurry, the concentrated sodium aluminate solution is cooled and seeded with gibbsite crystals, causing gibbsite to

15   crystallise from solution. The gibbsite is calcined to produce alumina, while the depleted (or "spent") liquor is recycled to digest more bauxite.

During digestion, some of the caustic is consumed in undesirable reactions with impurities within the bauxite, reducing the liquor's productivity. One of the most significant of these

20   reactions results in the formation of sodium carbonate, arising from the dissolution of inorganic carbonates within the mineral phases present, or from the thermal and oxidative degradation reactions of organic compounds. Unless controlled, with each cycle of the liquor through the process the sodium carbonate concentration would continue to rise, with a corresponding reduction in the liquor's ability to digest gibbsite or boehmite from the

25   bauxite.

The most common technique for controlling the sodium carbonate concentration in Bayer process liquors is to causticise using either quicklime or slaked lime. This process can be carried out either within the digestion circuit itself (by introducing lime with the bauxite), or

30   more commonly, as a side-stream process. The addition of lime directly with bauxite is not common except where lime is required to control other impurities (such as titanium or

-2-

phosphorus), because the very concentrated liquors contribute to poor efficiency. Unless the temperature is very high, most of the lime undergoes side-reactions with the aluminate in solution to yield calcium aluminate species, particularly tricalcium aluminate (TCA, often also referred to as C3A in the cement industry).

5

In the more prevalent side-stream causticisation, a dilute liquor stream (usually taken from one of the mud washing stages) is reacted with a slaked lime slurry, generally at close to the atmospheric boiling point of the combined liquor. Alternatively, the slurry is sometimes added directly to the mud washer. The amount of sodium carbonate converted and the

10   efficiency of lime utilisation are dependent upon many variables, but in most refineries, the lime efficiency is in the vicinity of 50 to 70%.

In the alumina industry it is common to refer to a Bayer liquor's carbonate impurity level in terms of the caustic to soda ratio, or 'C/S'. Here, 'C' refers to the sum of the concentrations

15   of sodium aluminate and sodium hydroxide, expressed as the equivalent concentration of sodium carbonate. The 'S' concentration refers to the sum of 'C' and the actual sodium carbonate concentration, this sum once again being expressed as the equivalent concentration of sodium carbonate. It can be seen from this that a fully causticised (carbonate-free) Bayer process liquor will possess a C/S ratio of 1.00. Typically, the C/S

20   ratio of the concentrated liquor stream in many alumina refineries is in the range 0.8 to 0.85. C/S ratios higher than this are difficult to achieve, because causticisation processes in current use are incapable of fully removing all of the sodium carbonate in the liquor streams fed to them. For example, a liquor with an S concentration of 135 g/L will typically only causticise to a C/S ratio of about 0.890. This limitation arises because the traditional

25   implementation of the causticisation reaction with slaked lime is controlled by a number of complex equilibria, including a competing reaction involving the aluminate ion in which TCA is formed.

By contrast, the causticisation reaction of pure mixed solutions of sodium carbonate and

30   sodium hydroxide with slaked lime is quite simple. The final concentration of hydroxide and carbonate ions is a function of the activities of the various ionic species present, in

- 3 -

equilibrium with the solid phases calcium hydroxide and calcium carbonate. The reaction can be described by the following equation:

$$Ca(OH)_2 + Na_2CO_3 \leftrightarrow CaCO_3 + 2NaOH \qquad \qquad ...(1)$$
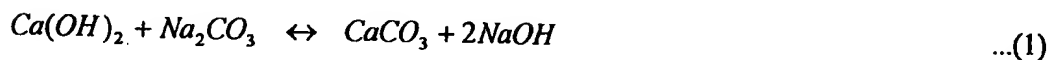
5

It has generally been assumed that the above reaction also applies when causticisation is performed in Bayer process liquors. However, it has been known for some time that calcium hydroxide reacts readily with the aluminate ion, ostensibly to form TCA. The formation of TCA is commonly held to occur via one or both of two mechanisms: a

10 simultaneous competitive reaction in which the calcium hydroxide reacts directly with the aluminate ion to form TCA [Chaplin,. N.T., Light Metals (1971), 47-61], or a "reversion" reaction in which the calcium carbonate formed during causticisation reacts with the aluminate. However, some authors have suggested that in Bayer liquors causticisation occurs via a "hydrated tricalcium aluminate intermediate" [Young, R.C., Light Metals

15 (1982), 97-117] or a "carboaluminate" phase [Lectard, A; Travaux ICSOBA, 12(17), (1982), 149-156] and that TCA forms as this material ages.

Irrespective of the mechanism proposed, causticisation as practised in the Bayer process has been inefficient in terms of the C/S achieved, and in the efficiency of lime use.

20 Furthermore, poor efficiency of lime utilisation has also meant that quite considerable amounts of aluminate ions are consumed in the formation of TCA. This can represent a substantial loss of alumina production.

A number of causticisation processes have been proposed over the years aimed at improved

25 lime efficiency. However, these processes are generally of limited value in that they are restricted to low 'S' concentration wash liquors, requiring large flows to be processed if sufficient mass of sodium carbonate is to be converted to compensate for the carbonate input to the refinery. In US Patent No. 2,992,893 a process is disclosed in which the thickened mud from a final mud washing stage was causticised, and then reacted with

30 supplementary sodium carbonate to recover some of the alumina lost in the formation of . TCA. The causticised liquor was then used in the mud washing stages. Apart from the 'S'

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concentration limitation, this process is not ideal in that a substantial proportion of the causticised liquor is lost with the red mud residue.

5   An improvement over this process is described in US Patent No. 3,120,996 in which causticisation is performed in a first stage washer, supplemented by further lime addition to a third stage washer. Higher lime efficiencies were achieved (approximately 85 to 95%), but only in quite dilute washer streams (80 g/L 'S'), and the achievable C/S ratio of the causticised liquor was not very high.

10   A later development disclosed in US Patent No. 3,210,155 involves the direct slaking of quicklime in a clarified wash liquor that had been heated to 100°C. After reaction, the slurry was then mixed with further wash liquor to encourage the reaction of TCA with sodium carbonate, and so recover alumina. While high C/S ratios were claimed with this process, it was restricted to wash streams with 'S' concentrations of approximately 15 to 40

15   g/L.

Another process was developed in Hungary in the 1980s by Baksa et al as disclosed in US patent No. 4,486,393. In this process, a red mud slurry from one of the washing stages was heated and fed to a reaction vessel with excess lime slurry. Apart from the "normal"

20   causticisation afforded in this tank, the excess lime reacted with sodalite and cancrinite desilication products to form a calcium hydrogarnet, releasing sodium hydroxide. The discharge from this vessel was then fed to a second vessel, and further reacted with a sodium carbonate solution. This solution was obtained by salting out sodium carbonate from concentrated solutions elsewhere in the plant. The reaction of sodium carbonate with

25   either the hydrogarnet or "hydrated" calcium aluminate resulted in the recovery of alumina and some caustic, although this step tended to reverse the gains made by formation of the hydrogarnet species. While an improvement over the basic causticisation principle, lime and alumina losses through the formation of TCA are still substantial, and the achieved C/S is still limited by the carbonate/hydroxide equilibrium reaction. Furthermore, efficiency

30   deteriorates badly if low 'S' concentration washer streams are not utilised.

- 5 -

In summary, it can be seen that the prior art causticisation methods suffer from deficiencies both in the extent to which Bayer process liquors can be causticised (i.e. the maximum C/S that can be achieved), and the efficiency with which lime is utilised to effect this causticisation. By virtue of their poor lime utilisation efficiency, these processes result in the loss of aluminate from solution, thereby reducing the alumina refinery's productivity. Further, the prior art methods are limited with respect to the concentration of the solutions that can be causticised, becoming very inefficient with liquors approaching typical first stage mud washing liquors, or mud settler overflow liquors.

SUMMARY OF THE INVENTION

The present invention was developed with a view to providing a process and apparatus for improved causticisation of Bayer liquors which is less susceptible to some of the disadvantages of the prior art noted above.

According to one aspect of the present invention there is provided an improved process for the causticisation of Bayer liquors in an alumina refinery, the process including the steps of:

reacting lime with aluminate ions in a Bayer liquor under controlled conditions of low to moderate temperature to form substantially only a hydrocalumite species and hydroxyl ions; and,

heating said hydrocalumite species in contact with a Bayer liquor under controlled conditions so as to cause the hydrocalumite species to react with the liquor to form calcium carbonate, aluminate ions and hydroxyl ions, whereby a causticised Bayer liquor is obtained and wherein the efficiency of lime utilisation is substantially increased and alumina losses minimised.

Typically the first reaction involving the formation of a hydrocalumite slurry is performed at temperatures between about 25°C and 100°C. Preferably, best performance with most Bayer liquors is obtained if the temperature is maintained between about 70°C and 80°C. Preferably the first reaction occurs in a Bayer liquor which is subject to agitation.

Preferably the second reaction involving the heating of the hydrocalumite species is

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performed at temperatures between about 100°C and 180°C. Most preferably the second reaction is performed under conditions of low shear at about 120°C.

Advantageously the process further includes the step of adding a suitable inhibitor to the Bayer liquor at a suitable point prior to heating the hydrocalumite species whereby undesirable reaction of the hydrocalumite species to form TCA is inhibited. Preferably said inhibitor is a complexing agent and/or surfactant which is capable of being adsorbed at active sites on the surface of the hydrocalumite species to restrict the diffusion of active species at these sites. Examples of suitable surfactants include sugars such as sucrose and glucose, and polysaccharides such as starch. Most preferably anionic organic surfactants are employed. Examples of anionic organic surfactants includes the following materials, their salts, and derivatives: any anionic homopolymers or copolymers (e.g. polyacrylic acid and its co-polymers with acrylamide, or polymers bearing hydroxamate functional groups), hydroxamic acids, humic and tannic acids, lignosulphonates, fatty acids, sulphonated carboxylic acids, carboxylic acids, and polyhydroxy carboxylic acids.

Advantageously the Bayer liquor employed in the first reaction involving the formation of the hydrocalumite species has been pre-causticised whereby the C/S ratio of the pre-causticised liquor can also be further increased.

Preferably the first reaction is performed in a Bayer liquor with a moderately high A/C ratio and low free caustic. A suitable liquor will typically have an "S" concentration of between 40 and 350 g/L, and an A/C ratio of between 0.2 and 0.95. More preferably the liquor will have an "S" concentration of between 120 and 160 g/L, and an A/C ratio greater than 0.55. Typical residence time required for the completion of the first reaction is between 5 and 30 minutes, in the presence of a suitable inhibitor.

Advantageously, the hydrocalumite slurry formed in the first reaction is subject to solid/liquid separation and the hydrocalumite solids reacted with a fresh liquor to be causticised via said second reaction.

- 7 -

According to a still further aspect of the present invention there is provided an improved process for the causticisation of Bayer liquors in an alumina refinery, the process including the steps of:

5   adding a suitable inhibitor to a Bayer liquor to stabilize the formation of a hydrocalumite species during causticisation to inhibit undesirable reaction of the hydrocalumite species to form TCA, whereby the attainable C/S ratio of the liquor can be increased.

Preferably said inhibitor is a complexing agent and/or surfactant which is capable of being 10   adsorbed at active sites on the surface of the hydrocalumite species to inhibit the diffusion of active species at these sites. Examples of suitable surfactants include sugars such as sucrose and glucose, and polysaccharides such as starch. Most preferably anionic organic surfactants are employed. Examples of anionic organic surfactants includes the following materials, their salts, and derivatives: any anionic homopolymers or copolymers (e.g. 15   polyacrylic acid and its co-polymers with acrylamide, or polymers bearing hydroxamate functional groups), hydroxamic acids, humic and tannic acids, lignosulphonates, fatty acids, sulphonated carboxylic acids, carboxylic acids, and polyhydroxy carboxylic acids.

Preferably the improved process further comprises the step of heating the liquor during 20   causticisation to temperatures within the range 100°C to 180°C. More preferably the liquor is heated to between 120°C and 140°C.

According to a further aspect of the present invention there is provided an improved process for the causticisation of Bayer liquors in an alumina refinery, the process including the steps 25   of:

obtaining a pre-causticised Bayer liquor; and,

reacting lime with aluminate ions in said pre-causticised Bayer liquor under controlled conditions of low to moderate temperature to form substantially only a hydrocalumite species and hydroxyl ions whereby the C/S ratio of the pre-causticised liquor 30   can be further increased.

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According to another aspect of the present invention there is provided an apparatus for the improved causticisation of Bayer liquors in an alumina refinery, the apparatus including:

a conventional reactor for causticising a Bayer liquor; and

a trim reactor for reacting lime with aluminate ions in the causticised Bayer

5   liquor under controlled conditions of low to moderate temperature to form substantially only a hydrocalumite species and hydroxyl ions whereby the C/S ratio of the causticised liquor can be further increased.

According to a still further aspect of the present invention there is provided an apparatus for

10   the improved causticisation of Bayer liquors in an alumina refinery, the apparatus including:

a primary reactor for reacting lime with aluminate ions in a Bayer liquor under controlled conditions of low to moderate temperature to form substantially only a hydrocalumite species and hydroxyl ions; and

15   a secondary reactor wherein said hydrocalumite species have been subject to heating in contact with a Bayer liquor under controlled conditions so as to cause the hydrocalumite species to react with the liquor to form calcium carbonate, aluminate ions and hydroxyl ions, whereby a causticised Bayer liquor is obtained and wherein the efficiency of lime utilisation is substantially increased and/or alumina losses are minimised.

20

Typically said primary reactor is a stirred tank reactor in which adequate mixing of the lime and the Bayer liquor occurs to promote the first reaction.

Typically said secondary reactor is a stirred tank reactor. Alternately a pressurised tube

25   reactor may be employed.

Preferably the apparatus further comprises means for separating the solid hydrocalumite species and the liquor from the primary reactor before reacting the hydrocalumite species in the secondary reactor with a fresh liquor.

30

Most preferably the liquor causticised in the secondary reactor is used as the feed liquor for

-9-

the primary reactor, whereby the C/S ratio of the causticised liquor can also be substantially increased.

BRIEF DESCRIPTION OF THE DRAWINGS

5   In order to facilitate a more detailed understanding of the nature of the invention several embodiments of the improved causticisation process and apparatus will now be described in detail, by way of example only, with reference to the accompanying drawings, in which:

Figure 1 is a simplified conceptual flow diagram of a basic implementation of the improved
10   causticisation process according to the invention;

Figure 2 is a simplified conceptual flow diagram illustrating a further implementation of the improved causticisation process according to the invention;

15   Figure 3 is a conceptual flow diagram illustrating an enhancement of the process illustrated in Figure 2;

Figure 4 is a conceptual flow diagram illustrating a further enhancement of the process illustrated in Figure 3;

20

Figure 5 is a conceptual flow diagram of a preferred embodiment of the improved causticisation process according to the invention;

Figure 6 is a conceptual flow diagram of another embodiment of the improved
25   causticisation process according to the invention; and,

Figure 7 is a conceptual flow diagram of a still further embodiment of the improved causticisation process according to the invention.

30

- 10 -

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

The present invention is based on the discovery that the reaction of lime (either quicklime or slaked lime) in Bayer process liquors occurs via a series of sequential reactions. Surprisingly the inventors' findings indicate that the direct reaction of calcium hydroxide

5   with the carbonate ion as described in equation (1) does not occur to any appreciable extent. More significantly, they have found that by suitable manipulation of solution compositions and conditions of temperature and agitation, it is possible to separate these reactions into distinct steps that can be individually optimised. This optimisation can increase the efficiency of lime utilisation to 95% or greater.

10

Most significantly, the inventors have found that it is possible to capitalise on the very different equilibria that apply in each of these steps to substantially increase the efficiency of carbonate removal. The causticisation process disclosed can be operated in such manner that it is possible to achieve C/S ratios of close to 1.00, even in quite concentrated Bayer

15   process liquors. It is a very surprising finding of this work that the C/S ratios that can be achieved are greater even than that obtainable in pure aluminate-free sodium hydroxide/sodium carbonate solutions of equivalent concentration.

This combination of very high C/S ratios with high lime utilisation efficiencies, even with

20   relatively concentrated liquors, has never been possible using the prior art processes. This flexibility affords considerable scope to apply the process in novel ways in the alumina refinery, using liquor streams that would not be feasible to treat with the prior art processes. While not wishing to be bound by theory, it is thought the following sequence of reactions takes place.

25

Reaction 1

The inventors have found that in solutions containing both sodium aluminate and sodium hydroxide, calcium hydroxide first reacts to form a lamellar calcium aluminate structure, the interlayer regions of which are filled with charge balancing ions and water molecules.

30   Similar species produced under very different reaction conditions have been reported in the cement industry literature [Fischer, R, and Kuzel H.J., Cement and Concrete Research, 12,

(1982), 517-526], where they are designated as C4A compounds. The structures are similar to the naturally occurring mineral hydrocalumite and this name has been used in some work for convenience [Perotta, AJ, and Williams, F., Light Metals (1995), 77-87]. The term hydrocalumite will also be adopted throughout the present specification. This
5   hydrocalumite species forms very rapidly in almost any Bayer liquor. No essential difference in the chemistry of the process has been found when calcium oxide (quicklime) is used instead of calcium hydroxide, as the slaking reaction appears to take precedence. However, the efficiency of the reactions using quicklime is poorer than when slaked lime is used, evidently because the reaction products that form tend to inhibit the diffusion of
10   calcium to the particle surface. This results in some lime remaining unreacted.

The general form of the reaction in Bayer-type liquors when calcium hydroxide is used is shown in equation (2) below:

15
$$4Ca(OH)_2 + 2Al(OH)_4^- + 2X^- + nH_2O \leftrightarrow [Ca_2Al(OH)_6]_2X_2 \cdot nH_2O + 4OH^- \qquad ...(2)$$
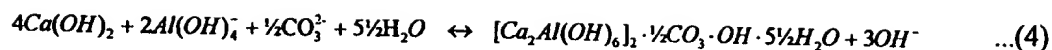
The charge balancing anions can be any of a number of species, denoted as X^- in the above equation. A number of species of this general form, varying only in the type and amount of charge balancing anions and interlayer water, have been identified on the basis of their
20   XRD patterns and by chemical analysis. In the absence of other anions (especially carbonate), the charge balancing species is commonly the hydroxyl ion, giving the following equation:

$$4Ca(OH)_2 + 2Al(OH)_4^- + 6H_2O \leftrightarrow [Ca_2Al(OH)_6]_2(OH)_2 \cdot 6H_2O + 2OH^- \qquad ...(3)$$
25
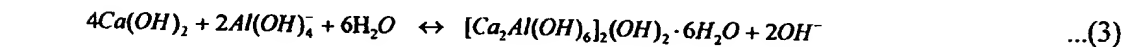
For convenience, hereinafter the species formed in this reaction will be referred to as hydrocalumite 0, or Hc0. Inspection of this reaction shows that while there is no net change in the 'C' concentration of the liquor, the alumina (A) concentration will fall due to the consumption of the aluminate ion. For liquors containing at least some carbonate, one of
30   the hydroxyl ions in the above structure is replaced by one half of a carbonate ion, as follows:

- 12 -

$$4Ca(OH)_2 + 2Al(OH)_4^- + \tfrac{1}{2}CO_3^{2-} + 5\tfrac{1}{2}H_2O \ \leftrightarrow \ [Ca_2Al(OH)_6]_2 \cdot \tfrac{1}{2}CO_3 \cdot OH \cdot 5\tfrac{1}{2}H_2O + 3OH^- \qquad \ldots(4)$$
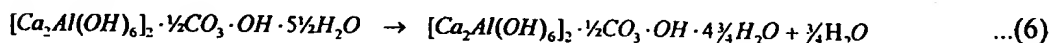
The species formed in this reaction is referred to hereinafter as hydrocalumite 1 (Hc1). Its
formation is a mildly causticising reaction. While two moles of aluminate are consumed per
mole of Hc1, *three* moles of hydroxyl ions are released. Thus, a net increase in 'C'
concentration of one mole of hydroxide per 4 moles of calcium hydroxide will be achieved.

Another reaction that has been reported in the literature involves the replacement of two of
the hydroxyl ions giving the following equation:

$$4Ca(OH)_2 + 2Al(OH)_4^- + CO_3^{2-} + 5H_2O \ \leftrightarrow \ [Ca_2Al(OH)_6]_2 \cdot CO_3 \cdot 5H_2O + 4OH^- \qquad \ldots(5)$$
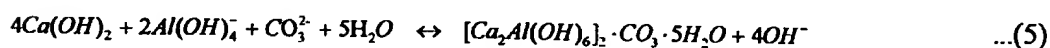
This is a more efficient causticising reaction, with 4 moles of hydroxyl ions released for
every two aluminate ions consumed. The net increase in 'C' concentration is thus two
moles of hydroxyl ions per 4 moles of calcium hydroxide. While the inventors have found
that a compound whose XRD pattern very closely matches the above species is involved in
the causticisation of Bayer liquors, the change in the solution's carbonate concentration
during its formation is inconsistent with the formula shown in equation (5). Thus, it is
unlikely that significant amounts of the material indicated in equation (5) are formed during
the reaction of lime in aluminate solutions. However, the amount of interlayer water in the
hydrocalumite structure is highly variable, and this alters the interlayer distance. A species
with a similar XRD pattern to that of the compound in equation (5) is known, and the
inventors propose that this species forms in Bayer liquors by the dehydration of Hc1
according to the following equation:

$$[Ca_2Al(OH)_6]_2 \cdot \tfrac{1}{2}CO_3 \cdot OH \cdot 5\tfrac{1}{2}H_2O \ \rightarrow \ [Ca_2Al(OH)_6]_2 \cdot \tfrac{1}{2}CO_3 \cdot OH \cdot 4\tfrac{3}{4}H_2O + \tfrac{3}{4}H_2O \qquad \ldots(6)$$

The species formed in this reaction will be referred to as hydrocalumite 2 (Hc2).

Typically, in the course of the reaction of the slaked lime, Hc1 will form first. As the
structure ages, often within minutes, a mixture of Hc1 and Hc2 will be produced. Later, as

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the reaction proceeds and carbonate in the liquor is depleted, only Hc0 will form and the final product will consist of mixtures of Hc1, Hc2 and Hc0. Owing to this dependency upon ageing and carbonate concentration, the precise proportions of Hc0, Hc1 and Hc2 so formed are difficult to estimate in advance. Other reaction conditions will also affect the

5   products to some extent. However, Hc1 is the predominant species formed under most conditions and this species can be used for the purposes of stoichiometry calculations.

The reaction of lime to form hydrocalumite is diffusion controlled, so that the rate of formation is thus not strongly affected by temperature. On the other hand, interconversion

10   between the Hc1 and Hc2 phases does seem to be temperature dependent.

Equations (4) through (6) are key observations in the development of this invention. Many previous studies have assumed the simultaneous formation of calcium carbonate and of TCA, which is caustic neutral, i.e. two hydroxyl ions are released for every two aluminate

15   ions consumed. In contrast, the above equations indicate that the formation of hydrocalumite can be used in the causticisation of Bayer liquors.

It is important to note that the causticising effect of hydrocalumite formation is not subject to the limiting effects of the carbonate/hydroxide equilibrium. Assuming no interference by

20   surface diffusion barriers, hydrocalumite formation will continue until either the calcium hydroxide or aluminate ions are almost completely consumed. To maintain charge neutrality, anions must be intercalated within the structure. Carbonate, the preferred anion, will thus continue to be absorbed into the structure until the material ceases forming, or almost all of the carbonate has been removed from solution. At low carbonate

25   concentrations, other anions may thus be intercalated within the structure, leading to a process for the causticisation of other impurity salts in Bayer liquors. This latter aspect is the subject of a co-pending patent application No. PP 9334.
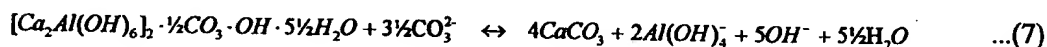
All of these hydrocalumite species are quite stable at low temperatures but become

30   increasingly unstable as the temperature rises. Apart from temperature, the rate of decomposition and the species that forms is also dependent upon the composition of the

- 14 -

solution with which they are in contact. The predominant decomposition reactions include a desirable reaction with carbonate ions in which calcium carbonate is formed, and an undesirable reaction in which TCA forms. However, if these compounds form while the calcium hydroxide particles are still reacting to form hydrocalumite, they may act as a

5   diffusion barrier and prevent full conversion. This effect can be overcome by adding a small amount of a suitable inhibitor, such as a complexing agent or surfactant (for example, sodium gluconate or sucrose), as will be discussed further below.

Reaction 2

10

The conditions under which the above species react to form calcium carbonate can be inferred from the following reaction mechanism:

$$[Ca_2Al(OH)_6]_2 \cdot \tfrac{1}{2}CO_3 \cdot OH \cdot 5\tfrac{1}{2}H_2O + 3\tfrac{1}{2}CO_3^{2-} \leftrightarrow 4CaCO_3 + 2Al(OH)_4^- + 5OH^- + 5\tfrac{1}{2}H_2O \qquad ...(7)$$

15

This is the main causticising reaction, and in conventional causticisation processes will begin almost immediately upon formation of the hydrocalumite. Inspection of the above equation shows that in this reaction, each mole of Hc1 reacts with 3.5 moles of carbonate to produce 4 moles of calcium carbonate, and releases 5 hydroxyl ions, together with 2 moles

20   of aluminate. Thus, any aluminate consumed during the formation of the hydrocalumite (be it Hc0, Hc1 or Hc2) is released again in this reaction.

Consequently, in a conventional causticisation reaction, it is observed that the alumina concentration falls very rapidly, normally accompanied by a slight rise in C/S,

25   corresponding to the formation of hydrocalumite. This is then followed by a slower but much greater rise in C/S, together with an increase in alumina concentration, as the reaction described in equation (7) proceeds.

The reaction of hydrocalumite with carbonate ions to form calcium carbonate is favoured

30   by conditions of high carbonate concentration, low aluminate concentration and low . hydroxide concentration. It is important to note that the reaction is under chemical control,

- 15 -

and is thus relatively unaffected by agitation conditions. However, the rate is strongly influenced by temperature, with the rate increasing by approximately one order of magnitude (10-fold) for every 6 to 8 degrees increase in temperature. Consequently, the inventors have found that at 103°C the reaction can take up to approximately 2 hours to come to completion, but only a few minutes at 120°C.

It is also important to note that the extent of this reaction will be controlled by the equilibria between the solids and the various species in solution. Consequently, the maximum achievable C/S will be a function of the activities of the carbonate, hydroxide and aluminate ions. Inspection of equation (7) shows that the equilibrium is much more strongly affected by the hydroxide concentration than the aluminate concentration, so it is of some benefit if the liquor fed to this process has a high A/C ratio (i.e., low free caustic). This can be facilitated by ensuring that the hydrocalumite is not formed in the liquor to be causticised, since this reaction will lower the A/C. However, the rate of equation (7) is impaired if the aluminate concentration is too high. A preferred A/C range is between 0.5 and 0.7.
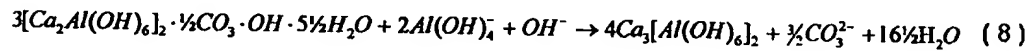
Increasing the temperature also drives the equilibrium towards the products of this reaction, allowing a higher C/S to be reached. The rate of the reaction is also substantially increased. This is particularly beneficial with high A/C ratio liquors. However, if the temperature is too high efficiency will suffer because the rate at which TCA forms, while not strongly temperature dependant, does increase with rising temperature. Consequently, best performance will be achieved with a liquor with a moderately high A/C ratio, and at a temperature of between 120°C and 140°C.

Reaction 3

The final reaction to consider is the formation of TCA. TCA ($Ca_3[Al(OH)_6]_2$) has a similar chemical formula to the hydrocalumites, and it is reasonable to consider that this species may react under the appropriate conditions to form TCA. Indeed, this seems to be the case: The inventor's experimental evidence suggests that hydrocalumite reacts with aluminate and hydroxyl ions to form TCA. It does not appear to be important which of the Hc species

- 16 -

described previously (Hc0-Hc2) is involved in this reaction. Consequently, using Hc1 as an example, it is believed the following reaction describes the formation of TCA:

$$3[Ca_2Al(OH)_6]_2 \cdot \tfrac{1}{2}CO_3 \cdot OH \cdot 5\tfrac{1}{2}H_2O + 2Al(OH)_4^- + OH^- \rightarrow 4Ca_3[Al(OH)_6]_2 + \tfrac{3}{2}CO_3^{2-} + 16\tfrac{1}{2}H_2O \quad (8)$$

This reaction is favoured by high aluminate and hydroxide concentrations and low carbonate concentration. These conditions are met towards the conclusion of the conventional causticisation process, which may explain the appreciable losses of lime to TCA, and the steady fall of C/S over time if the residence time in the causticiser is excessive. Furthermore, the above reaction appears to be under diffusion control – agitation and the presence of a large hydrocalumite surface area strongly affects the rate of formation of TCA, but it is less strongly affected by increasing temperature. Thus, a suitable balance of high temperatures and gentle agitation during the main causticisation reaction (equation 7) will decrease TCA formation (and improve efficiency) because the rate of consumption of hydrocalumite to form calcium carbonate greatly exceeds the rate of its reaction to form TCA.

By considering the reactions described above, it is clearly possible to develop a process in which the desirable steps are optimised, while the undesirable reactions are minimised. This is not feasible in a single tank (unless the tank is operated in batch mode and the conditions varied during the course of the reaction), because each of these steps requires mutually incompatible conditions to operate efficiently. In all prior art processes, the individual steps of the causticisation reaction are not identified or optimised in this way. Consequently, the causticisation process as currently practised is an unsatisfactory compromise between acceptable lime and alumina losses and extent of causticisation.

Design Principles

In developing an improved causticisation process, the inventors have identified the following design principles:

- 17 -

Slaked lime or quicklime is preferably first reacted with aluminate ions to form only the lamellar C4A structure (the hydrocalumite), in a well agitated reactor (the Primary Causticisation Reactor). The exact nature of this reactor is not critical, and any system which provides adequate mixing of the reactants will suffice. To ensure that this occurs

5   with no residual unreacted lime, and to prevent calcium carbonate or TCA formation, certain conditions must be met. The reaction should occur under conditions of low to moderate temperature (between 25 and 100°C). The exact upper limit is a function of the alumina, carbonate and free hydroxide concentrations, but best performance with most liquors is obtained if the temperature is maintained between 70°C and 80°C. Best

10   performance is obtained with a liquor with a moderately high A/C ratio and low free caustic. If too high a temperature is chosen, or too high free caustic concentration, there is a tendency for the reaction to be impeded by the formation of TCA, which acts as a diffusion barrier. This will tend to prevent full reaction of the calcium hydroxide, producing particles with a core of unreacted lime, reducing the efficiency of the reaction. The carbonate

15   concentration is less important, but the lower the carbonate concentration, the lower the maximum temperature at which this step in the process can be operated. Suitable liquors will have an 'S' concentration of between 40 and 200 g/L (preferably between 120 and 160 g/L), and an A/C ratio of between 0.2 and 0.95 (preferably greater than 0.55). The residence time required for the completion of this reaction is typically between 5 and 30 minutes.

20   However, if the correct liquor composition and temperature are used, longer residence times will have no discernible negative effects.

In a typical application of the principles described so far , the hydrocalumite and the liquor in contact with it are then heated to force the reaction described in equation (7) to proceed.

25   The slurry should be heated as hot as practicable. In a continuous system, this will necessitate transfer of the slurry to a second reactor (the Secondary Causticisation Reactor). In a simple non-pressurised stirred tank, the liquor should preferably be heated to close to the boiling point of the slurry. Agitation in such a system must be given special consideration. If the agitation is vigorous, hydrocalumite will react with aluminate and

30   hydroxyl ions forming TCA and causing a loss of efficiency. Preferably, a low-shear plug flow reactor (such as a tube reactor) will be employed operating at temperatures between

- 18 -

100 and 180°C, although best performance will be obtained at about 120°C. The precise residence time required to react the hydrocalumite formed in step 1 is dependent upon many factors, especially the temperature and presence of surfactants. However, a typical stirred tank reactor operating at approximately 103°C will require in the vicinity of 2 hours to reach completion, while approximately 15 minutes will be required in a tube reactor operating at 120°C.

Ideally, the slurry formed in step 1 should be filtered or some other means of separating the solid and liquid employed. The solids should then be reacted with a fresh liquor to be causticised.

Ideally, the liquor causticised in the Secondary Causticisation Reactor should be used as the feed liquor for the Primary Causticisation Reactor. This will ensure that the A/C ratio of the liquor feeding the Primary Reactor is high. More importantly, it permits even higher C/S ratios to be achieved, as the formation of the hydrocalumite is a causticising reaction. Since this reaction is not subject to the same equilibria as that occurring in the Secondary Reactor, it is possible to achieve C/S ratios of close to 1.00 in this reactor if sufficient lime is added.

Effect of Additives

During the course of the development of this process, the inventors found that if suitable inhibitors were added, the undesirable reaction of the hydrocalumite to form TCA could be greatly reduced, without appreciably influencing the reaction of Hc with carbonate to form calcium carbonate. This results in greater maximum C/S values being achieved, with higher efficiency of lime utilisation and greater ease of use. This arises because the reaction of hydrocalumite with aluminate and hydroxyl ions to form TCA is diffusion controlled (equation 8), while the reaction of Hc with carbonate is not (equation 7). Consequently, compounds that adsorb at active sites at the Hc surface will inhibit the diffusion of active species at these sites, retarding the reaction. On the other hand, while the presence of these adsorbed molecules may also partially inhibit the reaction with carbonate, the effect will be far less. This decrease in the rate of reaction of Hc with carbonate can be suitably overcome

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by enhancing any of the factors known to improve the causticisation reaction, of which increasing the temperature is probably the most effective and simple to achieve.

Virtually any class of surfactant can be used in this context, providing it adsorbs to the hydrocalumite structure. For example, sugars such as sucrose and glucose, and polysaccharides such as starch can be used. However, the inventors have found that anionic organic surfactants are most effective. A non-exclusive list of examples of this class of compound includes the following materials, their salts and derivatives: any anionic homopolymers or copolymers (e.g. polyacrylic acid and its co-polymers with acrylamide, or polymers bearing hydroxamate functional groups), hydroxamic acids, humic and tannic acids, lignosulphonates, fatty acids, sulphonated carboxylic acids, carboxylic acids, and polyhydroxy carboxylic acids.

The addition of the inhibitor can be made at any point prior to or within the Secondary Causticisation Reactor. Thus, the inhibitor may be added with the lime or liquor to be causticised, into the Primary Reactor, or into the secondary Reactor itself. It is also possible to dose the inhibitor into other locations within the Bayer refinery, provided that a significant proportion of the material reports to the causticiser. Addition prior to the Primary reactor greatly enhances the crystallinity of the hydrocalumite, and tends to produce hydrocalumite almost exclusively of the Hc1 variety (in the presence of adequate carbonate). However, while this enhanced crystallinity appears to have some benefit, the preferred dosing point is to the Secondary Reactor, whereupon good causticisation results are obtained with minimum consumption of inhibitor.

The use of an inhibitor also appears to improve the performance of conventional (prior art) causticising circuits. The presence of the inhibitor stabilises the hydrocalumite as it forms, preventing the usual simultaneous side-reaction that leads to the formation of TCA. Significant improvements in lime utilisation efficiency and liquor causticity can thus be achieved by dosing a suitable inhibitor at any point prior to the causticisation reactor, or into the reactor itself. However, the rate of the causticising reaction is also partially inhibited and allowance must be made for this either by increasing the residence time

- 20 -

within the reactor, or, more preferably, by increasing the temperature. The applicable temperature range, as with the process disclosed within this patent, is between approximately 100°C and 180°C, preferably between 120°C and 140°C.

5   The amount of inhibitor to be dosed is dependent upon the nature of the inhibitor and the location of its addition point into the causticisation circuit. Thus, the dose rate for a particular inhibitor must be determined by experiment. Examples of the action of inhibitors and their associated dosages are reported elsewhere in this document.

10   The invention is further described and illustrated by the following examples. These examples are illustrative of a variety of possible implementations and are not to be construed as limiting the invention in any way. In each of the following described examples dosing with a suitable inhibitor will provide enhanced performance.

15   **Example 1**

A basic implementation of an improved causticisation process based on the first of the above design principles is shown in Figure 1. In this system a conventional causticiser is employed as the primary reactor 5 and the secondary causticiser 8 is used to form the hydrocalumite species. This system utilises dosing of lime slurry to both the primary and

20   secondary causticisers. Because the hydrocalumite formation occurs in the second reactor, and is not further utilised, this configuration does not exhibit high lime utilisation efficiency. However, it represents a simple method of boosting the C/S ratio of a liquor, effectively adding "trim" causticisation to a conventional causticiser.

25   Best performance is obtained by first causticising the liquor using a high temperature tube digestor for the primary causticiser 5, followed by plate or flash cooling 6 to between 20° to 100°C, more preferably between 70 to 80°C. Agitation conditions within the secondary or "trim" causticiser 8 are not critical, although the tank's contents should preferably be completely suspended. The amount of lime required in this reactor will depend upon the

30   level of C/S boost required, and can be determined from the stoichiometry described by equation (4).

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In the example given here, the Hc formed in the "trim" causticiser 8 is filtered 9 and combined with the waste lime products from the Primary causticiser 5, both of which are then disposed of. An alternative is to use the Hc to effect further causticisation, improving

5   lime utilisation efficiency and recovering aluminate ions. This can be achieved by directing the solids to another reaction vessel fed with a fresh liquor stream to be causticised, however a more preferable embodiment of the invention is disclosed in Example 2.

10   **Example 2**

A typical implementation of the improved causticisation process based on the first two of the preceding principles is shown in Figure 2. In this system, a lime source (preferably a paste or slurry of slaked lime, although quicklime can be used) is fed together with the liquor to be causticised into a primary reactor vessel 10. Primary reactor 10 may be an in-

15   line mixer, tubular reactor or stirred tank. Agitation conditions within this reactor 10 are not critical, although the reactor's contents should be completely suspended. In this system, the vessel 10 is typically a stirred tank reactor and the liquor to be causticised will typically be a first or second washer overflow, as indicated in Figure 1, although the process is in no way restricted to these. The applicable range of 'S' concentration should be in the range of 40 to

20   250 g/L, although best performance is obtained for 'S' concentrations between 80 and 160 g/L. Improved performance is obtained for liquors with high A/C ratios. The temperature in this tank should be between 20 and 100°C, although best performance is obtained at between 70 and 80°C. The residence time in this tank should be approximately 5 to 20 minutes, but extended residence times of 2 hours or more have little appreciable deleterious

25   effect. The purpose of this reactor is to react the lime to form pure Hc1, with little or no unreacted lime, calcium carbonate or TCA.

The slurry is then fed to a heater 12 and heated. If existing causticisation equipment is utilised, the slurry should be heated to just below the atmospheric boiling point of the

30   slurry. For most washer overflow liquors, this will be in the range 102°C to 105°C. Preferably, however, the slurry is heated to higher temperatures, typically between

- 22 -

approximately 100°C and 180°C, more preferably to between 120°C and 140°C. The discharge from the heater 12 is fed to a secondary reactor 14, in which agitation conditions are controlled such that the solids are just suspended. This reactor 14 can be CSTR, but ideally it will be a plug flow reactor. Under the above conditions, a residence time of

5   approximately 2 hours will be required at approximately 103°C, and about 10 minutes at 120°C. The products of this tank are cooled (if required) and fed to a solid/liquid separation device 16 such as a settling tank, centrifuge, or preferably a filter.

The causticised liquor is returned to the process. Typically this would involve returning it to

10   the mud settler or mixing it in a tank with the clarified settler overflow liquor. The reacted lime solids can be disposed of, but since they are almost exclusively calcium carbonate, they can alternatively be further washed and filtered to recover adhering soda. The solids can then be dried and calcined to regenerate calcium oxide for further use. The washings can be returned to the mud washing circuit, or used elsewhere in the plant.

15

This scheme improves the efficiency of lime utilisation by ensuring that very little lime remains unreacted due to the formation of surface materials capable of acting as diffusion barriers. The loss of alumina through the formation of TCA is also greatly decreased. However, the maximum achievable C/S using this system is equivalent to a conventional

20   causticisation process, unless elevated temperatures and/or an inhibitor are employed.

Example 3

Improved performance can be obtained by applying the third design principle – forming the hydrocalumite in another liquor, separating the solid product and liquor in a solid/liquid

25   separation device 18, and using the hydrocalumite cake as the causticising agent in a secondary tank 14 fed with a suitable liquor stream. A simple conceptual flow diagram depicting this process is shown in Figure 3. Similar plant components as in Figure 2 are identified with the same reference numerals.

30   In this configuration, the A/C ratio of the liquor feeding the secondary causticiser 14 is maintained at a high level. This is aided by the reaction of Hcl according to equation (7).

- 23 -

The high A/C ratio alters the equilibria in the secondary causticiser 14, permitting higher C/S ratios to be achieved. Of course, more lime is required to achieve these higher C/S ratios, but the lime efficiency is high, with low alumina losses. Some causticisation also occurs in the Primary Causticiser 10, contributing to the carbonate removal efficiency of the

5   system.

Example 4

A substantial improvement over the basic implementations described above is shown in

10 Figure 4. In this embodiment, all four of the design principles have been incorporated. Lime is fed into a reaction vessel 10 (primary causticisation tank) operating at between 40 and 100°C, more preferably 70 to 80°C, together with a proportion of the causticised stream from the secondary causticisation tank 14. By doing this, a stream with an enhanced A/C and low carbonate concentration is fed into the primary reactor 10. The lime reacts with the

15 aluminate ion to form the hydrocalumite species, and further causticises the liquor according to the reaction scheme described by equation (4) [and in some instances, possibly equation (5)]. The product thus formed is a pure hydrocalumite species containing a variable amount of carbonate, the extent depending upon the initial carbonate concentration of the liquor and the amount of lime added.

20

Under the conditions described above, the amount of unreacted lime in the discharge from the primary causticiser 10 is low. This hydrocalumite material forms the raw material for the secondary causticisation step, and is separated from the now highly causticised liquor produced in the Primary Causticiser 10. The causticised liquor is then returned to the plant

25 at a suitable location, such as the mud settlers or polishing filters. The separation step can be effected using any solids/liquid separation device 18 including gravity settling, cycloning, or centrifugation, but best performance is obtained by filtration. This filtration is simple to achieve, as the morphology of the solids obtained in this step facilitates easy separation.

30

The filtered cake is reslurried with the clarified fresh liquor to be causticised in mixing tank

- 24 -

20. The temperature of this stream should be between 40 and 100°C, more preferably between 70°C and 80°C. The liquor can be any process stream with an 'S' concentration between 40 and 350 g/L as Na_2CO_3. However, best performance will be obtained with more dilute liquors with an 'S' concentration of between 100 and 160 g/L. The reslurried liquor is

5   then heated to close to the atmospheric boiling point of the slurry in heater 12 and directed to the secondary causticisation reactor 14, where it is held for between 30 minutes and 4 hours, preferably 2 hours at 103°C, during which time the reaction described by equation (7) occurs. The agitation conditions within this tank should be controlled such that all of the solids are suspended, but excessive agitation should be avoided to minimise the formation

10 of TCA. Preferably, a plug flow reactor is used although a stirred reactor vessel is quite adequate.

The reacted slurry is then pumped to a solid/liquid separation device 22 such as a gravity settler, cyclone, centrifuge or preferably filter. The solids may be discarded, however the

15 very high efficiency of the process (producing almost pure calcium carbonate) as described in all of the Examples other than Example 1 allows the solids to be washed (and the washings returned to the mud washing circuit) and calcined to re-generate the quicklime. Thus, the consumption of quicklime by the refinery can be substantially reduced using this process.

20

A portion of the clarified liquor from the second stage causticisation reactor 14 is split and directed to the primary causticisation reactor 10 to form the hydrocalumite species. Best causticisation performance will be obtained by directing the entire flow to the Primary causticiser tank 10, but this will require greater filtration capacity. Performance is enhanced

25 using this technique, because the products of reaction will contain more hydrocalumite 2. The amount of lime to be added is calculated from the requirements of the Secondary Causticisation reactor 14. This can be estimated from the stoichiometry shown in equation (7), and from the calculated carbonate /hydroxide/ aluminate equilibrium for the liquor to be causticised.

30

Clearly, given the relative causticising efficiencies of equations (4) and (7), less lime will be

- 25 -

required to achieve the calculated C/S ratio in the secondary reactor than would be required to fully causticise the liquor in the Primary reactor. However, if some loss of lime efficiency and alumina can be tolerated, it is possible to use this process to causticise the liquor to very high C/S ratios by overcharging the Primary causticiser with lime.

5

Example 5

The performance of the system can be further enhanced by conducting the secondary causticisation process at elevated temperatures (between 100°C and 180°C). Best performance is obtained at about 120°C. The preferred embodiment of this process is shown in Figure 5.

10

In this system, the slurry from the mixing tank is directed to a heat exchanger 24 where the temperature is raised to 120°C. The slurry is then passed through a secondary pressure reactor, preferably a tube reactor 26, with a residence time of 5 to 40 minutes, preferably 15 minutes. Longer residence times may be required in the presence of an inhibitor, depending upon its nature. By operating at this temperature, and using this configuration, the efficiency of the reaction of the hydrocalumite to form calcium carbonate is greatly enhanced, while the formation of TCA is greatly inhibited.

15

20   ### Example 6

The efficiency of the process of Example 5 falls as the C/S of the plant liquor approaches or exceeds the carbonate/hydroxide/aluminate equilibrium value in the Secondary causticiser. At some point, a steady state will be achieved at which the input of carbonate to the plant is balanced by the ability of the causticisation process to remove it. In most circumstances this will not be a problem, as the plant C/S ratio achievable using this process will be very high. However, if higher C/S ratios are required, this can be achieved by overcharging lime to the Primary Causticiser 10, as indicated in the previous Example. The problem with this is that if the C/S of the liquor feeding the secondary causticiser is too high for reaction (7) to proceed, the lime utilisation efficiency will be poor, and alumina will be lost.

25

30

This situation can be corrected using the enhancement shown in Figure 6. In this process,

- 26 -

the flow of liquor to the Secondary Causticiser 14 is supplemented by a stream 28 that is rich in sodium carbonate. This can be supplied in various ways, such as via a salting out evaporator, as Trona (to supplement existing caustic input to the plant), or by linking the discharge from an oxidative organics removal process, such as wet oxidation or

5   electrolysis. In this way, the process can efficiently causticise the sodium carbonate in these streams, as well as recovering all of the alumina that would otherwise be lost. The lime efficiency can be restored to greater than 90% in this way. It should be noted that by using this process, it is possible to increase the refinery's C/S to close to 1.00, depending upon the amount of carbonate produced in the digestion circuit and the size of the units employed.

10

Experimental Results

Effect of Inhibitors

A number of inhibitors representative of the classes of compound described earlier were

15   examined for their impact on causticisation in a series of batch tests. These tests loosely simulate the prior art causticisation process, and serve only to demonstrate the advantages of the use of inhibitors in this regard. An inhibitor that performs well in these tests is even more effective when used at the correct dose in the proposed improved causticisation process.

20

The tests were conducted in 500 mL polypropylene bottles to which 450 mL of a first washer overflow liquor pre-heated to 97°C were added. The composition of the liquor prior to addition of the lime slurry and additive is shown in Table 1 below.

25   **Table 1: Composition of 1st washer overflow liquor**

A (g/L)	C (g/L)	S (g/L)	A/C	C/S
81.1	122.5	151.0	0.662	0.811

A lime slurry consisting of 58g of an industrial grade hydrated lime (90.3% available lime as $Ca(OH)_2$) in 216 mL of deionised water was prepared and heated to 97°C. 30mL of this

- 27 -

slurry was added to each of the bottles, together with sufficient of the appropriate additive to give a 1 g/L concentration in the resultant mixture. The bottles were sealed and tumbled end-over-end in a thermostatically controlled water bath at 97°C. These agitation conditions are far less vigorous, and the temperature somewhat lower, than is typical of industrial conditions. This, together with the retarding effect of the additives themselves on the causticisation reaction rate, required extended residence times to be used. The results of the bottle tests taken after 360 minutes of reaction are shown in Table 2.

Table 2: Liquor composition after 360 minutes reaction.

Additive	A (g/L)	C (g/L)	S (g/L)	A/C	C/S	Lime Efficiency
None	67.6	119.3	131.8	0.567	0.905	68%
Sucrose	69.1	121.5	131.8	0.569	0.922	80%
Commercial hydroxamate copolymer	67.4	120.3	131.4	0.560	0.916	75%
Polyacrylate (MWt<1M)	67.8	119.3	131.2	0.568	0.909	71%
Commercial polyacrylate (MWt>1M)	67.7	120.1	131.4	0.564	0.914	74%

These results clearly show the advantages of inhibitors in Bayer causticisation, both in increased liquor causticity (C/S) and efficiency of lime utilisation. Through suitable optimisation of additive dose rate, causticiser residence time and reactor temperature, substantial improvements in causticisation performance can be achieved, even when applied to the prior art causticisation processes. However, these advantages are particularly pronounced when applied to the improved causticisation process disclosed in this document.

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C mparison of Improved Causticisation Process with Prior Art

A series of batch causticisation tests were conducted in the laboratory to demonstrate the improved performance and advantages of the proposed causticisation process. The prior art process was also simulated for the purposes of comparison.

5

<u>Prior Art Example</u>

The prior art process was simulated by batch reaction in a 3.75 litre Parr reactor. First washer overflow liquor (1.795 litres) was added to the reactor and heated to 100°C. A slurry of an industrial grade hydrated lime (32.7g) in 203 mL of deionised water was

10   pre-heated to 95°C, before addition to the reactor. This amount of lime was calculated to achieve a target C/S of 0.950 (assuming 100% efficiency). After addition of the lime slurry, the reactor was sealed and permitted to react at 100°C under thermostatic control for three hours. Agitation was applied using twin pitched-blade turbine impellers operating at 200 rpm. Samples of both the liquor and solids were taken at regular

15   intervals. Liquor samples were analysed for A,C and S and total sodium content. Solids were analysed for their elemental composition by XRF, and for their CO_2 content by acidification and measurement of the evolved gas.

<u>Prior Art Example – Effect of Inhibitor</u>

20   The test procedure described above was repeated, with the addition of 0.1 g/L of sodium gluconate to the first washer overflow liquor. Additional residence time was provided to compensate for the effect of the inhibitor on the rate of the causticisation reaction.

The effect of the inhibitor on the prior art process can be seen by referring to Tables 3

25   and 4 below. The data shown are for samples taken at the maximum C/S for each case: for the Prior Art example, this occurred at approximately 45 minutes residence time in the reactor. In the case of the test in which inhibitor had been added, a similar C/S was achieved at 45 minutes but continued to rise until a maximum was reached at between 260 and 330 minutes.

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Table 3: Effect f Inhibitor on Prior Art Causticisation Perf rmance

Sample	A (g/L)	C (g/L)	S (g/L)	A/C	C/S	TS (g/L)
Start liquor	92.7	138.8	170.6	0.668	0.813	227.1
Prior Art	81.9	137.8	155.2	0.594	0.888	207.0
Prior Art + inhibitor	82.6	141.8	154.7	0.583	0.917	205.8

Table 4: Typical Solids Analyses at Maximum C/S (% dry weight)

Sample	CaO	Al_2O_3	CO_2	Other	Lime Efficiency
Prior Art	50.6	9.2	20.6	19.6	54.3%
Prior Art + inhibitor	52.6	3.8	31.0	12.6	78.6%

The lime efficiency was calculated on the basis of the CO_2 content divided by the CaO content, expressed as a molar ratio and corrected for the available lime and alumina content of the original hydrated lime.

It can be seen that the addition of the inhibitor has resulted in a dramatic increase in the efficiency of lime utilisation, reflected both in the much higher maximum C/S and the higher alumina concentration in the causticised liquor. This latter aspect is also apparent from the solids analysis, which shows that substantially lower alumina losses are incurred. These outcomes are achieved, however, at the expense of a much longer reaction time, which can be overcome either by providing additional causticiser tank volume or by raising the reaction rate by increasing the temperature. However, better performance is obtained by using one of the preferred embodiments described in the Examples.

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Improved Causticisation process (Example 2)

The application of the improved causticisation process in a basic form (as described in Example 2) was simulated by batch reaction in a 3.75 litre Parr reactor. The simulation consisted of two parts – formation of hydrocalumite at 80°C, followed by rapid heating and reaction of the mixture to 120°C. Owing to the high thermal mass and slow heating rate of the Parr reactors, it was necessary to react the lime in a reduced volume of liquor at 80°C, and then add the remaining liquor at a much higher temperature to achieve rapid heating of the mixture to 120°C.

First washer overflow liquor (500 mL) was added to the reactor and heated to 80°C. A second Parr reactor of two litre capacity was filled with first washer overflow liquor (1.500 litres) and heated to 185°C. A slurry of an industrial grade hydrated lime (38.01g) in 210 mL of deionised water, preheated to 80°C, was added to the 500 mL of liquor in the first reactor. This amount of lime was calculated to achieve a target C/S of 0.950 (assuming 100% efficiency). The reactor was immediately sealed and permitted to react under thermostatic control at 80°C for ten minutes. Agitation was applied using twin pitched-blade turbine impellers operating at 200 rpm. At the conclusion of the ten minute reaction, during which hydrocalumite was formed, the contents of the second reactor were transferred under pressure to the first reactor. Upon mixing, the combined temperature of the liquor and slurry in the first reactor was 120°C. This temperature was maintained thereafter by thermostatic control. The mixture, still agitated at 200 rpm, was permitted to react for 90 minutes. Samples of both the liquor and solids were taken at regular intervals. Liquor samples were analysed for A,C and S and total sodium content. Solids were analysed for their elemental composition by XRF, and for their CO_2 content by acidification and measurement of the evolved gas.

Improved Causticisation process (Example 2) – Effect of Inhibitor

The test procedure described above was repeated, with the addition of 0.5 g of sodium gluconate to the 3.75 litre reactor at the end of the 10 minute hydrocalumite formation stage. This gave a final concentration of approximately 0.25 g/L in the combined liquor

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during the main causticisation reaction.

A similar test using sucrose as inhibitor was also conducted. In this instance, the sucrose
was added at the commencement of the reaction, at a concentration of 2.0 g/L in the
5   combined liquor.

Typical results from each of the above tests are summarised in Tables 5 and 6 below,
showing the liquor and solids analyses respectively. The results are compared with a
repeat test of the Prior Art process for reference. In each case, the results shown
10   represent the highest C/S achieved during the reaction. For the prior art process, this
was achieved after 45 minutes of reaction, whereas for the Improved Process without
inhibitor only 2 minutes was required. A similar C/S was also achieved in two minutes
in the case of the Improved Process to which inhibitor was added, however the C/S
continued to rise well beyond this point, finally reaching a maximum after
15   approximately 45 to 60 minutes.

20   Table 5: Typical liquor analyses at maximum C/S

Sample	A (g/L)	C (g/L)	S (g/L)	A/C	C/S	TS (g/L)
Start liquor	86.8	133.9	166.4	0.648	0.805	229.0
Prior Art	77.1	134.5	152.5	0.573	0.882	200.9
Example 2	77.3	136.1	151.7	0.568	0.897	207.1
Example 2 + inhibitor	78.8	141.2	152.8	0.558	0.924	208.0

25   Table 6: Typical solids analyses at maximum C/S (% dry weight)

Sample	CaO	Al_2O_3	CO_2	Other	Lime Efficiency
Prior Art	50.6	9.2	20.8	19.4	54.8%
Example 2	51.6	6.6	26.6	15.2	68.8%

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| Example 2 + inhibitor | 52.8 | 3.6 | 34.4 | 9.2 | 86.9% |

The lime efficiency was calculated on the basis of the CO_2 content divided by the CaO content, expressed as a molar ratio and corrected for the available lime and alumina content of the original hydrated lime.

The liquor chosen to demonstrate the process is of a higher 'S' concentration than is typically used for causticisation in most Bayer process refineries. The reason such a liquor would not normally be used for this purpose is apparent from the lime efficiency results shown in Table 6. The lime efficiency shown for the Prior Art process (54%) was obtained from a sample drawn at the maximum C/S for the reaction and therefore represents the maximum efficiency obtained. This optimum is rarely achieved in industrial practice, so the efficiency would normally be substantially less than this.

By contrast, a higher maximum C/S and substantially improved lime efficiency are observed for the Example 2 process. Maximum C/S is achieved rapidly (2 minutes) and remains there for approximately a further 8 minutes before reversion becomes significant.

Even more striking is the result for the Example 2 process to which an inhibitor (sodium gluconate) had been added. In this case, a far higher maximum C/S was achieved, at over 30% greater lime efficiency than the Prior Art process. Moreover, reversion is extremely slow: after a further 30 minutes at temperature, the C/S had fallen only 0.002 points. Similar results were obtained for the test in which sucrose was used as the inhibitor, achieving an identical C/S of 0.924 but at a slightly lower lime efficiency of 84.0%. However, the time required to achieve maximum C/S using sucrose (5 minutes) is considerably less than with sodium gluconate.

Apart from the very clear advantages of much increased liquor C/S and high lime efficiency, this Example demonstrates the tolerance of the process to high liquor concentrations and variations in residence time. In combination, these factors contribute

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to improved stability of causticisation in the Bayer refinery. Furthermore, alumina losses caused by the formation of TCA are greatly reduced, which should contribute to improved refinery productivity.

5   Improved Causticisation Process (Example 5)

The application of the improved causticisation process in its preferred embodiment (as described in Example 5) was simulated in the laboratory by conducting a series of sequential batch reactions in a 3.75 litre Parr reactor. Each cycle of the series consisted of two steps: formation of the hydrocalumite at 80°C in a pre-causticised liquor (the

10   Primary causticisation reaction), and preparation of this pre-causticised liquor using the hydrocalumite so formed (the Secondary Causticisation reaction).

To initiate a series of cycles, several litres of first washer overflow liquor were first causticised with a slurry of industrial grade hydrated lime (90.3% available lime as

15    $Ca(OH)_2$) using a conventional (prior art) causticisation process. After filtration and disposal of the collected solids, this provided a precausticised liquor from which the initial sample of hydrocalumite could be produced.

Two litres of this liquor was placed in the 3.75 litre Parr reactor and the temperature

20   raised to 80°C, maintained under thermostatic control. The required quantity of hydrated lime to achieve a target C/S of 0.950 (at 100% efficiency) was slurried with hot deionised water in a 500 mL polypropylene bottle, equilibrated at 80°C, then quantitatively transferred to the Parr autoclave to initiate the reaction. Agitation was applied using twin pitched-blade turbine impellers operating at 200 rpm. After allowing

25   30 minutes for the reaction to conclude, the entire contents of the reactor were filtered under vacuum using a Buchner funnel and filter flask. Residual solids and liquor remaining in the Parr reactor were washed into the filter funnel with hot deionised water. The filter cake was further washed with hot deionised water to remove entrained liquor (this procedure, while unnecessary in normal use, was required to facilitate

30   calculation of the mass balance).

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First washer overflow liquor (500 mL) was added to the reactor and heated to 80°C. A second Parr reactor of two litre capacity was filled with first washer overflow liquor (1.500 litres) and heated to 185°C. The damp hydrocalumite cake prepared in the previous step was added to the 500 mL of liquor in the first reactor. The reactor was immediately sealed and the agitator switched on to disperse the solids. After allowing approximately two minutes for dispersal of the solids and thermal equilibration, the contents of the second reactor were transferred under pressure to the first reactor. Upon mixing, the combined temperature of the liquor and slurry in the first reactor was 120°C. This temperature was maintained thereafter by thermostatic control. The mixture, still agitated at 200 rpm, was permitted to react for 2 minutes.

After reaction, a sample of the slurry was collected and immediately filtered through a 0.45μm Supor filter membrane. The filtrate was analysed for A,C and S and total sodium content. Solids were thoroughly washed with deionised water on the filter. Damp cake was collected for examination by XRD. The remaining solids were dried under partial vacuum (104 mm Hg) at 105°C and analysed for their elemental composition by XRF, and for their CO_2 content by acidification and measurement of the evolved gas.

The contents of the reactor were transferred to a pressure filter equipped with a 0.45μm Supor filter. The filtrate was collected to be used to initiate the next cycle of the process. Some loss of liquor occurred due to sampling and transfer of the slurry. Allowance was made for this in the subsequent cycle by adjusting the lime charge in the primary causticisation reaction, and by reducing the volume of first washer overflow liquor in the secondary causticisation reaction. This procedure was repeated until four full cycles of the process were completed.

Improved Causticisation Process (Example 5) – Effect of Inhibitor

The test procedure described above was repeated, with the addition of 1.0 g of sodium gluconate with the hydrocalumite to the 3.75 litre reactor at the start of the secondary causticisation reaction. This gave a final concentration of approximately 0.5 g/L in the

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combined liquor during the secondary causticisation reaction. To compensate for the retarding effect of the inhibitor, a residence time of 120 minutes was allowed for the secondary reaction.

5   Improved Causticisation Process (Example 5) – Maximum C/S

To demonstrate the ability of this process to achieve very high liquor causticity (C/S), the above procedure was repeated with a higher lime charge, calculated to achieve a target C/S of 1.00. The test procedure described above was repeated, with the addition of 1.0 g of sodium gluconate with the hydrocalumite to the 3.75 litre reactor at the start

10   of the secondary causticisation reaction. This gave a final concentration of approximately 0.5 g/L in the combined liquor during the secondary causticisation reaction. To compensate for the retarding effect of the inhibitor, and to allow the reaction sufficient time to achieve the much higher C/S target, a residence time of 150 minutes was allowed for the secondary reaction.

15

Typical results from each of the Example 5 tests described above are summarised in Tables 7 and 8 below, showing the liquor and solids analyses respectively. The results are compared with the Prior Art process test data for reference.

20

Table 7: Typical liquor analyses at maximum C/S

Sample	A (g/L)	C (g/L)	S (g/L)	A/C	C/S	TS (g/L)
Start liquor	92.4	138.3	170.2	0.668	0.813	231.7
Prior Art	81.9	137.8	155.2	0.594	0.888	207.0
Example 5	80.5	137.6	151.2	0.585	0.910	199.0
Example 5 + inhibitor	81.1	143.5	153.9	0.565	0.932	199.9
Example 5: maximum C/S	80.0	144.5	151.3	0.554	0.955	200.0

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Table 8: Typical solids analyses at maximum C/S (% dry weight)

Sample	CaO	Al$_2$O$_3$	CO$_2$	Other	Lime Efficiency
Prior Art	50.6	9.2	20.6	19.6	54.3%
Example 5	51.8	6.6	25.4	16.2	65.4%
Example 5 + inhibitor	52.6	2.8	35.9	8.7	91.1%
Example 5: maximum C/S	52.2	3.8	33.1	10.9	84.6%

It can be seen from the above results that the preferred embodiment of the process, as described in Example 5, offers significant advantages over the Prior Art process both in the achievable C/S and the efficiency of lime utilisation. In the above example, lime efficiency exceeded 91%. The preferred embodiment also offers advantages over that of Example 2. With no additive present, the lime utilisation efficiency is similar to that of Example 2, but achieves a much higher C/S ratio (0.910 versus 0.897). With inhibitor present, both improved lime efficiency (91.1% versus 86.9%) and higher C/S ratio (0.932 versus 0.924) are achieved. However, the most important advantage of the preferred embodiment over that described in Example 2 may be seen by referring to the results for the test in which maximum C/S was targeted. Using the preferred embodiment of the process, it is possible to achieve extremely high liquor causticity (C/S of 0.955 or better), still with markedly improved lime efficiency (better than 80%) over the prior art process. Higher liquor causticity than this can be achieved, at the expense of progressively degraded lime efficiency.

From the preceding examples and the description of several possible implementations, it will be apparent that the improved process of causticisation disclosed herein has many significant advantages over causticisation technology as currently practised. These include:

[a]   The lime utilisation efficiency is extremely high (over 90% is achievable), even with quite concentrated liquors.

[b]   The achievable C/S ratio is substantially increased (in excess of 0.955), even with quite

5   concentrated liquors, allowing higher plant caustic concentrations and improved productivity. Even higher C/S ratios are achievable at the expense of some loss of lime efficiency.

[c]   A comparatively pure calcium carbonate waste product is produced, creating the potential to recycle lime via a small lime kiln, with further potential reductions in lime consumption.

10   [d]   The loss of alumina due to the formation of unwanted calcium aluminate species is greatly reduced. The recovery of alumina from bauxite is improved, resulting in increased production.

[e]   Causticisation is generally much faster, resulting in reduced tank volumes, and a more compact installation.

15   [f]   Performance is stable, despite variations in liquor composition and flows.

Reduced indirect carbon dioxide emissions due to improved refinery efficiency, and reduced lime wastage.

[g]   Simple to implement at virtually any refinery.

[h]   Reduced volume of residue due to minimal lime consumption – potential savings in

20   residue disposal and storage costs.

[i]   Potential to distribute the causticisation reaction piecewise over two or more of the refinery's liquor streams.

[j]   Potential to implement multiple causticisation processes at various locations in the refinery.

25

Now that several embodiments of the invention have been described in detail, it will be apparent to persons skilled in the chemical engineering arts that numerous variations and modifications can be made without departing from the basic inventive concepts. All such modifications and variations are considered to be within the scope of the present invention, the nature of which is to

30   be determined from the foregoing description and the appended claims. Furthermore, the preceding examples are provided to illustrate specific embodiments of the invention and are not intended to limit the scope of the process of the invention.

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THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS

1.   An improved process for the causticisation of Bayer liquors in an alumina
refinery, the process including the steps of:

5   reacting lime with aluminate ions in a Bayer liquor under controlled
conditions of low to moderate temperature to form substantially only a hydrocalumite
species and hydroxyl ions; and,

heating said hydrocalumite species in contact with a Bayer liquor under
controlled conditions so as to cause the hydrocalumite species to react with the liquor to
10   form calcium carbonate, aluminate ions and hydroxyl ions, whereby a causticised Bayer
liquor is obtained and wherein the efficiency of lime utilisation is substantially increased
and alumina losses minimised.

2.   An improved process for the causticisation of Bayer liquors as defined in
15   Claim 1, wherein the Bayer liquor employed in the first reaction involving the formation of
the hydrocalumite species has been pre-causticised whereby the C/S ratio of the pre-
causticised liquor can also be further increased.

3.   An improved process for the causticisation of Bayer liquors as defined in
20   claim 2, wherein the first reaction is performed in a Bayer liquor with a moderately high
A/C ratio and low free caustic.

4.   An improved process for the causticisation of Bayer liquors as defined in
claim 3, wherein said Bayer liquor has an "S" concentration of between 40 and 350 g/L,
25   and an A/C ratio of between 0.2 and 0.95.

5.   An improved process for the causticisation of Bayer liquors as defined in
claim 4, wherein the liquor has an "S" concentration of between 120 and 160 g/L, and an
A/C ratio greater than 0.55.

30

6.   An improved process for the causticisation of Bayer liquors as defined in

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claim 5, wherein a residence time required for the completion of the first reaction is between 5 and 30 minutes, in the presence of a suitable inhibitor.

7.   An improved process for the causticisation of Bayer liquors as defined in claim 6, wherein the first reaction involving the formation of a hydrocalumite slurry is performed at temperatures between about 25°C and 100°C.

8.   An improved process for the causticisation of Bayer liquors as defined in claim 7, wherein best performance with most Bayer liquors is obtained if the temperature is maintained between about 70°C and 80°C.

9.   An improved process for the causticisation of Bayer liquors as defined in claim 8, wherein the first reaction occurs in a Bayer liquor which is subject to agitation.

10.   An improved process for the causticisation of Bayer liquors as defined in claim 1, wherein the second reaction involving the heating of the hydrocalumite species in contact with a Bayer liquor is performed at temperatures between about 100°C and 180°C.

11.   An improved process for the causticisation of Bayer liquors as defined in claim 10, wherein the second reaction is performed under conditions of low shear at about 120°C.

12.   An improved process for the causticisation of Bayer liquors as defined in claim 1, wherein the process further includes the step of adding a suitable inhibitor to the Bayer liquor at a suitable point prior to heating the hydrocalumite species whereby undesirable reaction of the hydrocalumite species to form TCA is inhibited.

13.   An improved process for the causticisation of Bayer liquors as defined in claim 12, wherein said inhibitor is a complexing agent and/or surfactant which is capable of being adsorbed at active sites on the surface of the hydrocalumite species to restrict the diffusion of active species at these sites.

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14.   An improved process for the causticisation of Bayer liquors as defined in claim 13, wherein suitable surfactants include sugars such as sucrose and glucose, and polysaccharides such as starch.

15.   An improved process for the causticisation of Bayer liquors as defined in claim 13, wherein anionic organic surfactants are employed as said inhibitor.

16.   An improved process for the causticisation of Bayer liquors as defined in claim 15, wherein said anionic organic surfactants are selected from the group consisting of the following materials, their salts, and derivatives: any anionic homopolymers or copolymers (e.g. polyacrylic acid and its co-polymers with acrylamide, or polymers bearing hydroxamate functional groups), hydroxamic acids, humic and tannic acids, lignosulphonates, fatty acids, sulphonated carboxylic acids, carboxylic acids, and polyhydroxy carboxylic acids.

17.   An improved process for the causticisation of Bayer liquors as defined in claim 1, wherein the hydrocalumite slurry formed in the first reaction is subject to solid/liquid separation and the separated hydrocalumite solids are reacted with a fresh liquor to be causticised via said second reaction.

18.   An improved process for the causticisation of Bayer liquors as defined in claim 17, wherein the causticised Bayer liquor obtained from the second reaction involving the heating of the hydrocalumite species is subject to cooling and solid/liquid separation, and wherein at least a portion of the clarified liquor is returned to the first reaction.

19.   An improved process for the causticisation of Bayer liquors as defined in claim 18, wherein the solids separated from the Bayer liquor from the second reaction include substantially pure calcium carbonate which is recalcined to regenerate the lime, for re-use within the refinery, thereby further reducing the lime requirements of the refinery.

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20.   An improved process for the causticisation of Bayer liquors in an alumina refinery, the process including the steps of:

adding a suitable inhibitor to a Bayer liquor to stabilize the formation of a hydrocalumite species during causticisation to inhibit undesirable reaction of the
5   hydrocalumite species to form TCA, whereby the attainable C/S ratio of the liquor can be increased.

21.   An improved process for the causticisation of Bayer liquors as defined in claim 20, wherein said inhibitor is a complexing agent and/or surfactant which is capable of
10   being adsorbed at active sites on the surface of the hydrocalumite species to inhibit the diffusion of active species at these sites.

22.   An improved process for the causticisation of Bayer liquors as defined in claim 21, wherein suitable surfactants include sugars such as sucrose and glucose, and
15   polysaccharides such as starch.

23.   An improved process for the causticisation of Bayer liquors as defined in claim 21, wherein anionic organic surfactants are employed as said inhibitor.

20   24.   An improved process for the causticisation of Bayer liquors as defined in claim 23, wherein said anionic organic surfactants are selected from the group consisting of the following materials, their salts, and derivatives: any anionic homopolymers or copolymers (e.g. polyacrylic acid and its co-polymers with acrylamide, or polymers bearing hydroxamate functional groups), hydroxamic acids, humic and tannic acids,
25   lignosulphonates, fatty acids, sulphonated carboxylic acids, carboxylic acids, and polyhydroxy carboxylic acids.

25.   An improved process for the causticisation of Bayer liquors as defined in claim 20, wherein the improved process further comprises the step of heating the liquor
30   during causticisation to temperatures within the range 100°C to 180°C.

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26.   An improved process for the causticisation of Bayer liquors as defined in claim 25, wherein the liquor is heated to between 120°C and 140°C.

27.   An improved process for the causticisation of Bayer liquors in an alumina
5   refinery, the process including the steps of:

obtaining a pre-causticised Bayer liquor; and,

reacting lime with aluminate ions in said pre-causticised Bayer liquor under controlled conditions of low to moderate temperature to form substantially only a hydrocalumite species and hydroxyl ions whereby the C/S ratio of the pre-causticised liquor
10   can be further increased.

28.   An apparatus for the improved causticisation of Bayer liquors in an alumina refinery, the apparatus including:

a conventional reactor for causticising a Bayer liquor; and

15   a trim reactor for reacting lime with aluminate ions in the causticised Bayer liquor under controlled conditions of low to moderate temperature to form substantially only a hydrocalumite species and hydroxyl ions whereby the C/S ratio of the causticised liquor can be increased.

20   29.   An apparatus for the improved causticisation of Bayer liquors in an alumina refinery, the apparatus including:

a primary reactor for reacting lime with aluminate ions in a Bayer liquor under controlled conditions of low to moderate temperature to form substantially only a hydrocalumite species and hydroxyl ions; and

25   a secondary reactor wherein said hydrocalumite species have been subject to heating in contact with a Bayer liquor under controlled conditions so as to cause the hydrocalumite species to react with the liquor to form calcium carbonate, aluminate ions and hydroxyl ions, whereby a causticised Bayer liquor is obtained and wherein the efficiency of lime utilisation is substantially increased and/or alumina losses are minimised.

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30.   An apparatus for the improved causticisation of Bayer liquors as defined in

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claim 29, wherein said primary reactor is a stirred tank reactor in which adequate mixing of the lime and the Bayer liquor occurs to promote the first reaction.

31.   An apparatus for the improved causticisation of Bayer liquors as defined in claim 30, wherein said secondary reactor is a stirred tank reactor.

32.   An apparatus for the improved causticisation of Bayer liquors as defined in claim 30, wherein said secondary reactor is a pressurised tube reactor.

33.   An apparatus for the improved causticisation of Bayer liquors as defined in claim 29, wherein the apparatus further comprises means for separating the solid hydrocalumite species and the liquor from the primary reactor before reacting the hydrocalumite species in the secondary reactor with a fresh liquor.

34.   An apparatus for the improved causticisation of Bayer liquors as defined in claim 33, wherein the liquor causticised in the secondary reactor is used as the feed liquor for the primary reactor, whereby the C/S ratio of the causticised liquor can also be substantially increased.

1/3

washer o/f   lime slurry

cooling water

reacted lime solids
to waste or kiln

lime slurry

plate heat
exchanger

5

S / L

S / L   9

8

primary
causticisation
reactor

6

secondary
causticisation
reactor

Causticised liquor

FIG.1.

washer o/f   lime slurry

12

Steam

14

Causticised liquor

16

10

L / S

primary
causticisation
reactor

Heater

secondary
causticisation
reactor

reacted lime solids
to waste or kiln

FIG.2.

washer o/f   lime slurry

primary
causticisation
reactor

10

to process

18   L/S

12

Steam

Washer O/F

14

secondary
causticisation
reactor

Heater

Causticised liquor

16   L/S

reacted lime solids
to waste or kiln

FIG.3.

reacted lime solids
to waste or kiln

cooling water

22   S/L

Plate
Exchanger

Causticised liquor

lime slurry

10

18   L/S

12

14

washer o/f

20

primary
causticisation
reactor

steam

secondary
causticisation
reactor

Mixing Tank

FIG.4.

3/3

reacted lime solids
to waste or kiln

FIG.5.

reacted lime solids
to waste or kiln

FIG.6.

INTERNATIONAL SEARCH REPORT

A.	CLASSIFICATION OF SUBJECT MATTER

Int Cl[6]:   C01F 7/06

According to International Patent Classification (IPC) or to both national classification and IPC

B.	FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C01F 7/06

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
AU: IPC C01F 7/06

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPAT: (HYDROCALUMIT: OR BAYER: OR HYDROXYL:)

C.	DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 3120996 A (PORTER) 11 February 1964	
A	US 4486393 A (BAKSA et al) 4 December 1984	
A	US 4609534 A (THE et al) 2 September 1986	

X	Further documents are listed in the continuation of Box C		X	See patent family annex

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	Document defining the general state of the art which is not considered to be of particular relevance		
"E"	earlier application or patent but published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed	"&"	document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
19 October 1999	– 4 NOV 1999

Name and mailing address of the ISA/AU	Authorized officer
AUSTRALIAN PATENT OFFICE PO BOX 200 WODEN ACT 2606 AUSTRALIA E-mail address: pct@ipaustralia.gov.au Facsimile No.: (02) 6285 3929	JOHN DEUIS Telephone No.: (02) 6283 2146

INTERNATIONAL SEARCH REPORT

C (Continuation).	DOCUMENTS CONSIDERED TO BE RELEVANT	
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2992893 A (SOUDAN et al) 18 July 1961	
A	US 3210155 A (CAGNOLATTI et al.) 5 October 1965	

INTERNATIONAL SEARCH REPORT

Box 1	**Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)**

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:

   because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:

   because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:

   because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a)

Box II	**Observations where unity of invention is lacking (Continuation of item 3 of first sheet)**

This International Searching Authority found multiple inventions in this international application, as follows:

See attached sheet.

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims

2. ☒ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest   ☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Box II

The International application doe not comply with the requirements of unity of invention because it does not relate to one invention or to a group of inventions so linked as to form a single general inventive concept. In coming this conclusion the Intentional Searching Authority has found that there are two inventions:

1. Claims 1, 27, 28, 29 are directed to a process and apparatus for the causticisation of Bayer liquors in an alumina refinery wherein, lime is reacted with aluminate ions <u>under controlled conditions of low to moderate temperature</u> to form substantially only a hydrocalumite species and hydroxyl ions, whereby the c/s ratio of the pre- causticised liquor can be increased. The above process and apparatus is considered to comprise a first "special technical feature".

2. Claim 20 is directed to a process for the causticisation of Bayer liquors in an alumina refinery comprising the steps of <u>adding a inhibitor</u> to a Bayer liquor to stabilise the formation of a hydrocalumite species during causticisation to inhibit undesirable reaction of the hydrocalumite species to form TCA. It is considered the above process comprises a second "special technical feature".

Since the above-mentioned groups of claims do not share either technical features identified, a "technical relationship" between the inventions, as defined in PCT Rule 13.2 does not exist. Accordingly the International application does not relate to one invention as a single inventive concept.

INTERNATIONAL SEARCH REPORT

Information on patent family members

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member			
US	4486393	DE	3307036	HU	187654

END OF ANNEX